THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

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TECHNICAL PAPERS

For the 1952 Annual Meeting

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The 1952 Convention Committee of the American Leather Chemists Association is writing to you at this time to determine whether or not you will have any scientific papers to present at the annual meeting to be held at Swampscott, Massachusetts, Monday, June 2 through Wednesday, June 4.

In order to develop our program will you kindly forward the following information to Mr. F. D. Thayer, American Cyanamid Company, 1937 West Main Street, Stamford, Connecticut:

1) By March 15th, your statement that you plan to present a paper.

2) The title of the paper.

3) The amount of time desired for the presentation of the paper.

4) By April 1st, at the latest, a short abstract, in duplicate, suitable for program purposes.

We ask that your action be taken promptly so that we may arrange our program and be able to confirm without delay your place on the program.

Please be aware that a violation of certain fundamentals upsets the plan of the program. To prevent this, the following should be noted:

1) As a rule 30 minutes is allotted for each paper, using up to 20 minutes for the presentation and the remainder for discussion.

2) Present only the significant findings of the work. (Such items as the reviews of previous works and detailed description of procedure can be in the paper as published in the Journal and/or developed in discussion).

3) Being concise in your presentation allows more time for the discussion period without disturbing the schedule of the program.

May we remind you that papers presented at the annual meeting become the property of the Association and cannot be presented in other journals or trade magazines *without release* by the Editor of the Journal.

Please do not delay the forwarding of your intention to present a paper.

1952 CONVENTION COMMITTEE

January 2, 1952

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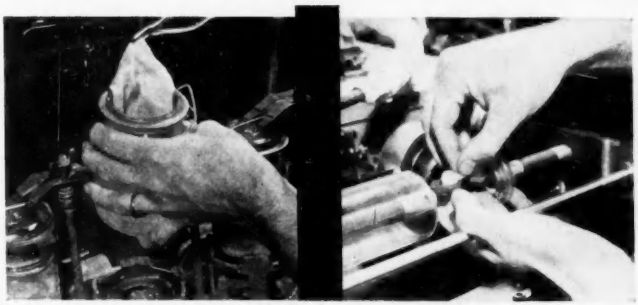

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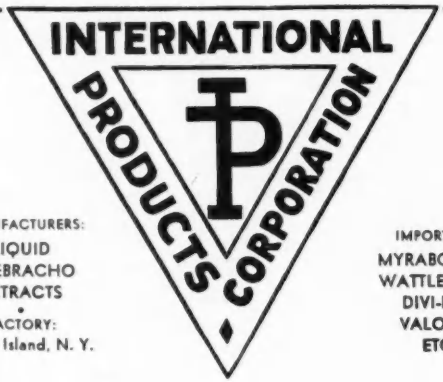

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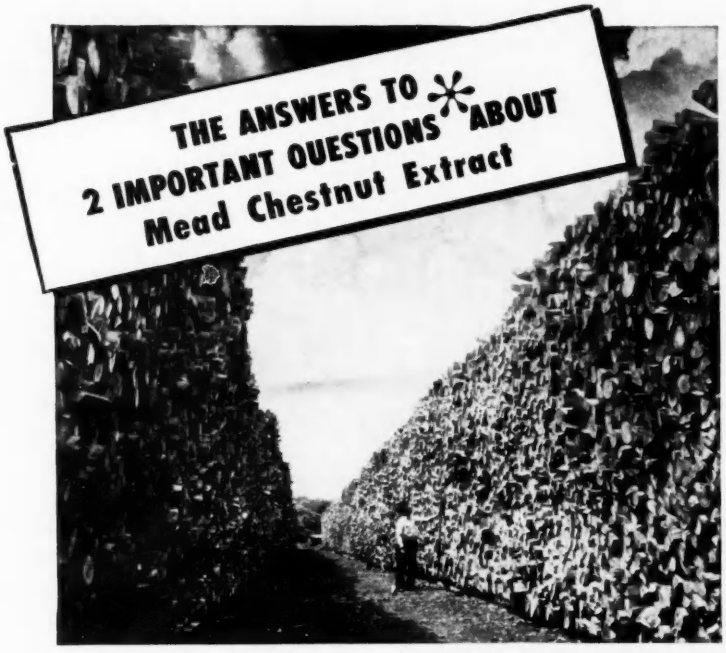

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B. Since the tanning system demands acid, the use of chestnut, with its plumping acidity, saves you money.

C. Mead Chestnut Extract eliminates up to 28% of leachhouse losses.

D. There are no hidden costs. When you use Mead Chestnut Extract, no time- and money-consuming preparation is required.

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Vegetable Tannin	Tan Yard Yield (*white weight basis*)
Chestnut Wood Extract	67%
Tanning Material A	61%
Tanning Material B	63%

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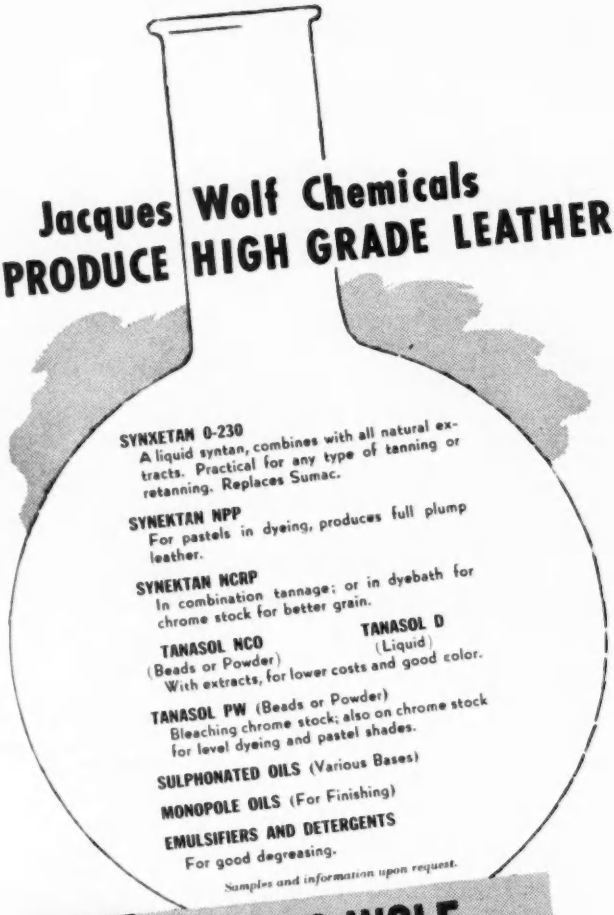

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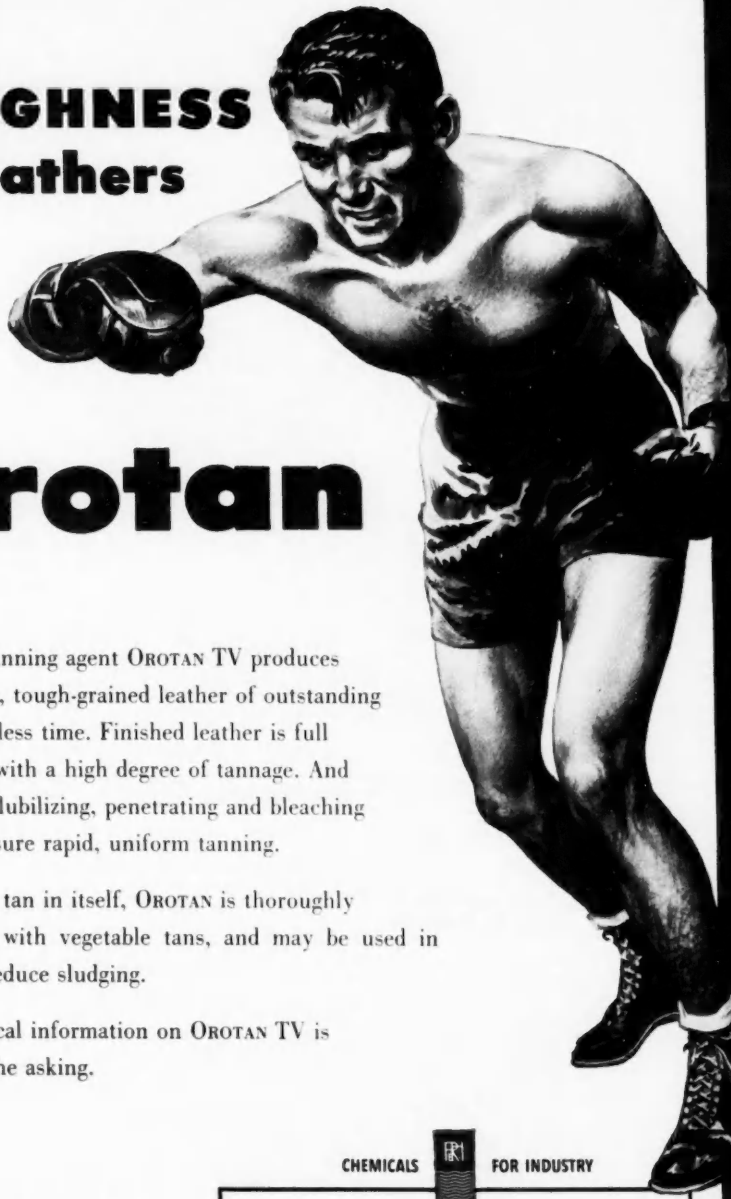

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M.P.	100°C

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ANALYSIS

Na_2S	60 to 62%
NaCl	1.5% Max.
Other Na Salts	2.0% Max.
Fe	8 ppm Max.
Cu, Ni, Cr, Mn, Pb	1 ppm Max.
Water of crystallization	35% Min.

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Mol. Wt.	56.1
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ANALYSIS

NaSH	70 to 72%
Na_2S	2.5% Max.
NaCl	0.8% Max.
Na_2SO_3 and $NaHCO_3$	0.4% Max.
Fe	5 ppm Max.
Cu, Ni, Cr, Mn, Pb	1 ppm Max.
Water of crystallization	28 to 26%

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JOURNAL OF THE
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VOL. XLVII JANUARY 1952 No. 1

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BUREAU OF EMPLOYMENT

Wanted: Chemist by Eastern Tannery, 25 to 30 years of age. Ph. D. preferred. Organic major with training in chemistry of polymers and resins. Good background in analytical both organic and inorganic. Leather experience preferable but not essential. Please give complete resume of past experience and qualifications along with personal data. Send replies to Box E W 50, Dr. Fred O'Flaherty, University of Cincinnati, Cincinnati 21, Ohio.

ACKNOWLEDGMENT BY AMERICAN CHEMICAL SOCIETY OF SYMBOLICAL SCROLL

Dr. R. M. Koppenhoefer
The American Leather Chemists Association
Socony-Vacuum Laboratories
412 Greenpoint Avenue
Brooklyn 22, New York

October 4, 1951

Dear Doctor Koppenhoefer:

The beautiful and symbolical scroll presented by The American Leather Chemists Association to the American Chemical Society on the occasion of our Diamond Jubilee is one of the valued mementos of this event. The celebration has left happy memories in the minds of thousands. In the years to come re-examination of the scrolls and gracious letters from our sister societies, presented at this time, will bring back these recollections.

I was gratified that your society could participate in the celebration of our seventy-fifth birthday. The American Chemical Society values the close relations which it has with other scientific and engineering organizations. This is particularly true with specialized organizations within the field of chemistry. There is great overlapping in our membership and many of our problems today are similar or identical.

Your society in the past has contributed significantly to our scientific knowledge. It is hoped that The American Leather Chemists Association and the American Chemical Society may advance together in the future both contributing increasingly to the well-being of our country.

Cordially yours,

N. H. Furman, *President.*

REPORT OF AUDITING COMMITTEE

Dr. Fred O'Flaherty, Secretary
American Leather Chemists Association
Campus Station
Cincinnati, Ohio

Dear Dr. O'Flaherty:

We have reviewed the books relative to the financial condition of the American Leather Chemists Association as of the calander year of 1950 and have found them to be consistent with the report made by Mr. Arthur W. Holmes, Public Accountant, in his audit of December 31, 1950.

Respectfully submitted,

F. L. Collins S. S. Kremen

REPORT ON LONDON CONFERENCE OF THE INTERNATIONAL UNION OF LEATHER CHEMISTS SOCIETIES

By H. G. Turley

I attended this meeting as a delegate from the American Leather Chemists Association. We had two delegates from America, the other being Dr. J. Kanagy from the National Bureau of Standards in Washington, D. C.

The first meeting of the Executive Committee, of which I am a member, was on Sunday afternoon, September 9th. Mr. Blockey, the President presided with Mr. A. Harvey as Secretary, and Dr. D. Burton as Treasurer. Amongst a number of matters was a request from the newly formed West German Society to enter the Union. This society is composed only in part of chemists which raised the problem of how dues should be assessed. We want to encourage the West German Society to join the International Union.

A Balance Sheet was presented and up to the present Conference the Union is in good condition.

The next place for the Conference was discussed and the offer of the A. L. C. A. to hold the 1953 meeting in Washington was debated. With reluctance this offer was declined because it was felt that only a handful of delegates would be able to attend for the practical reasons of the cost of the journey and difficulties of currency. The offer of the Nordic Society to hold the 1953 Conference in Stockholm was accepted, and for this, Dr. K. Gustavson was appointed first Vice-President to succeed Mons. Mallebay. Dr. Engeler of the Swiss Society was appointed to the Executive Committee. My appointment as a co-opted member of the Executive Committee was continued.

On the Sunday afternoon a reception was given by the Forestal Land, Timber & Railways Co., Ltd., at the Mayfair Hotel, London. This was well attended and formed a good introduction to the business of the Conference.

The meeting proper opened on Monday morning, September 10th with an appropriate ceremony at the Skinners Hall under the auspices of the Master of the Leather Sellers Company. The beautiful Leather Sellers Company Hall could not be used as it was destroyed by bomb action during the war. It was the Skinners Company that originally founded the Tanning School in Leeds of which Procter was the first distinguished Director. The Leather Sellers Company later founded the Leather Sellers Technical College which recently has become a National College.

About 200 members were present representing 15 Societies – which is an increase over the number represented at the first Conference in Paris two years ago.

The programme of papers was interesting and discussion was of a high order and stimulating to the members present. Many expressed their appreciation of the high quality of the discussions.

I am giving a short resume of some of the papers:-

The Influence of Fine Structure of Collagen Fibers in Tanning

By Dr. H. Phillips

Dr. Phillips who is Director of the B. L. M. R. A. gave a thought provoking paper pointing out the probable importance of the crystallinity of collagen fibrils bearing on some of the problems of tanning and dyeing. He came to this point of view with comparison to similar points of view held in industries utilizing other fibers, such as cellulose and wool.

Enzyme Unhairing

By G. Leger

Dr. Leger described experiments with papain for unhairing using principally thiourea as activator.

The Function of the Carboxyl Group of Collagen for Fixation of Cationic Chromium Complexes

By K. H. Gustavson

Dr. Gustavson gave an important paper on an investigation on chrome liquors with ion exchange resins. This was done in the acid and neutral condition. In the neutral condition the sodium in the resin is replaced by chromium. The overall results are considered to prove that chrome tanning is a cationic process in which the chromium reacts with the carboxyl groups of the protein.

Study of the Variation of the Physical and Chemical Properties of Chrome-tanned Leather

By J. R. Kanagy

Dr. Kanagy's paper was very clearly presented and favourably received. This part of the work with the National Bureau of Standards was conducted to determine the best manner of sampling for the examination of the numerous experiments in Army leather that have been made for the Quartermaster Department of the Army. In essence, Kanagy has found that the best test location is from a sample taken close to the backbone and close to the butt of a side. This position is somewhat close to the old "A" position of the A.L.C.A.

The Complexity of Tanning Extract Composition

By T. White, K. S. Kirby and E. Knowles

This was the description of some very exact work that has been carried on under Dr. White's direction for the Forestal Land, Timber & Railways

Co., Ltd., aimed at the elucidation of the composition and ultimately the structure of the vegetable tannins. White has tackled this by a combination of the methods of chromatography on paper and partition between solvents. They have separated 37 components from wattle, one-third of which are tans and have found that quebracho is even more complex. A highly important finding is that these vegetable tans consist of a large number of polyphenols. They owe their overall solubility to the mutual solubility of one compound on another. When purified, some of the compounds are actually insoluble, and the presence of even a trace of water is most important in studying solvent solubility. After fractionating the tannins on solvent columns further separations are obtained by paper chromatography.

White emphasizes the composition of a tannin and not its structure, and points out that the tanner may actually be using in a tanning blend more than 100 different products.

Paper Chromatography and Tannins

By H. KILCHHER

A second contribution on paper chromatography was given by Dr. Kilchher of the Geigy Company of Switzerland. Dr. Kilchher presented some colour diagrams showing the different bands of colour given under ultra-violet light by paper chromatography on different natural tans. He claims to be able to distinguish quickly natural tans and synthetic tans.

The Effect of Salts in Vegetable Tanning

By D. BURTON and J. M. HARRISON

This was a general paper presented by Professor Burton pointing out the importance of the salts and acids in vegetable tanning and making a plea for a common viewpoint in regard to vegetable and chrome tanning.

Lubricating Properties of Mineral Oils as Replacements for Fatty Oils in Fatliquoring

By R. M. KOPPENHOEFER

Dr. Koppenhoefer's paper was very well presented by M. E. Blane. Very briefly this work shows that it is possible to substitute some of the raw oil in a fatliquor by an equivalent quantity of suitable mineral oil.

On the third day the Conference journeyed to the new laboratories of the B.L.M.R.A. These laboratories have recently been installed in an old country mansion amidst delightful surroundings of ancient trees, spacious lawns and colorful glower gardens. The various divisions of the laboratories comprising about 14 departments were visited in turn under the direction of guides. The exhibits were beautifully set out and described by the head of the department who is an outstanding authority in his field—particularly impressive

to the writer were the exhibits on microscopy on leather fibers, chromatography, chemistry, physics and biochemistry. This is probably the outstanding leather research organization in the world today, and its developments have fully justified the vision and understanding of the early pioneers in Goverment-sponsored research after the first world war.

After visiting the laboratories a very fine lunch was tendered by Messrs. Barrow, Hepburn and Gale at Great Fosters—a fine old Elizabethan house.

After lunch a visit was made to Windsor Castle, the delegates being fortunate enough to see the Royal apartments. A delightful excursion followed up the River Thames. Due to a wet season the flowers and grass were in fine condition and never did the famous lawns of England appear greener, more luscious and brighter in the sunshine which shone for the greatest part of the journey. Of course, tea was served during the journey on the water.

After closing the Conference a banquet was held at the Park Lane Hotel, by the courtesy of the British Leather Chemists, through the Society of Leather Trades Chemists.

The banquet was a colorful affair conducted with great courtesy and the usual toasts to the King, the International Union of Leather Chemists Societies, the over-seas delegates, and, of course, the Ladies.

The official delegates to this International Union were as follows:-

French Society

PROF. P. CHAMBARD — CH. MONNET
A. BOIDIN — H. VOURLOUD
J. MALLEBAY

Swiss Society

E. BAUMANN — PROF. A. ENGELER

Belgian Society

A. FIEVEZ — G. KAMP

Italian Society

E. DURIO — G. BRAVO
P. BOCCIARDO

Spanish Society

A. GALLARDO — MISS M. PANIKER

Dutch Society

J. L. VAN GIJN — P. J. VAN VLIMMEREN
J. ROELOFS HEYRMANS

American Society

G. W. STANBERY — A. N. KAY — H. G. TURLEY
C. G. TELANDER — E. G. KEINER — W. B. HARRIS
R. M. KOPPENHOEFER — J. KANAGY

British Society

M. P. Balfe
J. R. Blockey
A. Harvey
D. Burton
C. F. Heal
G. H. W. Humphreys
P. S. Briggs

Nordic Society

J. A. Aabye
K. H. Gustavson
Aarne Hellemaa

Received Nov. 11, 1951

REPORT OF THE SUB-COMMITTEE ON DETERMINATION OF GREASE IN LEATHER - 1950-51

R. M. Lollar
Chairman of Sub-Committee

H. B. Merrill
Chairman of Committee on Pre-Tanning and Post-Tanning Processes

At the 1950 Annual Meeting, the Committee on Pre-tanning and Post-tanning Processes was directed to study a modified procedure developed by Zimmerman and Pangborn [1] for determining fats, oils, and related materials in leather. This procedure is embodied in a proposed change in Federal Specification KK-L-311, Method 6031 (1950) which is "in process of adoption" according to information received from personnel of the Bureau of Standards.

Apparatus

In Zimmerman's procedure, the leather is extracted with chloroform in the apparatus specified by the A. S. T. M. for determining grease in knit goods (see Reference 1, page 343). This apparatus works on the same principle as the Soxhlet apparatus, but the extraction is much more rapid. Because the siphon cup is small, and is surrounded by the vapor of the boiling solvent, the condensate siphons every two minutes, instead of about every 15 minutes as in the Soxhlet apparatus, giving 60 changes of solvent in 2 hours in contrast to 20 changes in 5 hours. Further, the A. S. T. M. apparatus is materially cheaper than the Soxhlet apparatus, and uses a considerably smaller charge of solvent. No comparative analyses have been made by this committee with the two forms of extraction apparatus, but the committee recommends the adoption of the A. S. T. M. apparatus as an alternate to the Soxhlet apparatus.

Sample Size

The sample used in the A. S. T. M. apparatus cannot exceed 5 grams. Such a sample is ample for determining the quantity of solvent-extractable

material, as 5 grams of a leather containing as little as 2 per cent grease will yield 100 mg. of extract, which should be weighable to ±1 mg. For leathers of high grease content, a 5 gram sample may actually be too large, because of the difficulty of drying fatty residues that weigh much more than 1 gram. This difficulty is enhanced when the 15 gram charge, currently authorized, is employed; such a charge may yield as much as 5 grams of extracted grease. In the opinion of the committee, the leather charge should be such that the weight of the extracted grease is from 0.1 to 1.0 g., which condition is fulfilled by using a 5 g. charge for leathers low in grease, and a 3 g. charge for heavily oiled or stuffed leathers. When a 15 gram charge must be degreased, prior to determining water solubles, this is best done as a separate operation, using a Soxhlet apparatus; the degreasing need not be complete, nor is it necessary to weigh the extracted grease.

Choice of Solvent

The essential difference between Zimmerman's method and the proposed change in Federal Specification KK-L-311 on the one hand, and the existing A. L. C. A. Method on the other, is the use of chloroform instead of petroleum ether. The question of choice of solvent for analytical determination of grease in leather has been argued off and on for a generation. In 1919, a committee headed by the late John Arthur Wilson [2] made extractions of 8 diverse leathers, fat liquored or stuffed with a variety of oils and greases. Each leather was extracted with 5 different solvents. Eleven analysts took part in the work. Invariably chloroform extracted the most, and petroleum ether the least material. A majority of the 1919 committee recommended the adoption of chloroform in place of petroleum ether as the official solvent, and this recommendation was repeated by a second committee in 1921 [3]. These recommendations were based on the well-founded belief that petroleum ether does not dissolve certain types of lipids, notably sulfated oils and oxidized fats. Failure to extract these materials not only gives a low result for fat, but also results in a fictitiously high result for fixed tannin. The opponents of the change argued [4], correctly, that chloroform extracts some materials other than fats and oils from some leathers. Among the materials mentioned were vegetable tannins, resins, rubber, sulfur, dyes, shellac, and nitrocellulose lacquers. No data was offered to show how much of any of these materials was actually extracted from any leather by chloroform. The proponents of chloroform believed that the errors due to incomplete extraction of fatty materials by petroleum ether were much more serious than the possible error caused by extraction of non-fatty material by chloroform; the opponents took the contrary view.

The recommendations of the 1919 and 1921 committees appear to have been tabled. However, in the intervening years, many laboratories have adopted chloroform as fat extractant, and the use of chloroform is prescribed

by various federal specifications [5], so that the proposed change in KK-L-311 is partially in effect already.

The present committee saw no reason to make further determinations of the difference in amount of material extracted by petroleum ether and chloroform. One member [6] attempted to find out how much, if any, tannin was removed by chloroform from vegetable tanned leather. Fat-free hide powders, tanned with chestnut, wattle, quebracho and eucalyptus extracts yielded negligible quantities of matter extractable by chloroform, but fat-free hide powder tanned with Orotan yielded a chloroform extract equal to about 2 per cent of the leather weight. This latter finding has been confirmed by Turley (private communication). This work indicates that extraction of vegetable tannin is not a source of appreciable error in the fat determination with chloroform, but reveals a new source of error,—namely, Orotan and possibly other syntans.

Probably no solvent exists that will remove quantitatively all fats, and substances resembling fats, from leather, without removing some of the numerous organic materials that may be present in some types of leather. The present committee feels that determination of matter extractable by chloroform is preferable to the determination of matter extractable by petroleum ether, as a general method. Accordingly, this committee recommended to the Council:

1. That the A. S. T. M. appartus proposed by Zimmerman be adopted as an alternate to the Soxhlet apparatus.
2. That chloroform replace petroleum ether as the prescribed solvent.
3. That the existing method [7] be revised accordingly.

These recommendations were approved by the Council, at a meeting held on June 10, 1951, subject to approval by the membership.

Drying Conditions

In drafting the proposed revision, the committee felt that conditions for drying the fatty residue "to constant weight" should be specified more closely. In the existing procedure "constant weight [is] defined as follows: *Reheat* (committee's italics) for one-half hour periods at 98 - 100° C. until the [weight] change is not greater than 1 per cent of the weight of the oil." This wording apparently permits an initial heating for any desired time, followed by reheating for one or more 30 minute periods until the loss (or gain) in weight is less than 10 mg. per gram of residue. We believe that many analysts merely dry the residue for what they consider an adequate time (one or two hours) and dispense with the reheating and reweighing. There is a tendency to heat longer than is necessary to remove moisture. This is undesirable, because every oil that we have studied either gains or loses weight continuously on prolonged heating, depending on the nature of the oil.

Merrill and Lollar, independently, carried out drying experiments with known weights of various oils, to which water and chloroform had been

added, to find out what heating time is required to obtain a dry weight equal to the weight of oil taken. Merrill's procedure was as follows: The water content, if any, of the oil was determined by the xylene distillation method. Approximately 1 gram of the oil was weighed (to 1 mg.) into each of 3 containers,—a tannin dish, a 300 ml. Soxhlet flask and a 400 ml. wide-mouth Erlenmeyer flask. The oil was dissolved in 10 to 15 ml. chloroform, and several drops of water were added. The mixture therefore resembled the residue obtained in a fat determination, after distilling off most of the solvent but before drying. Each flask or dish was heated on a boiling water bath until the odor of chloroform could no longer be detected; then the vessel was placed in an oven at 100 - 105° C for 30 minutes, desiccated for 30 minutes, and weighed. This was repeated 3 or 4 times. The sample weight (corrected for water, if any) was subtracted from each residue weight, and the algebraic differences were calculated as percentage of the sample weight.

Lollar's procedure was practically the same, except that he used aliquots of stock solutions of the oils, dissolved in chloroform. He allowed the chloroform to evaporate on a hot water bath. Lollar carried out each test in a Precision forced-draft oven at 100 - 105° C., in a still air oven at 100 - 105° C., and in a vacuum oven at 80 - 82° C. Merrill did no work with the vacuum oven, and relatively little work with the still air oven.

Merrill and Lollar used the same samples of a light mineral oil (Finish Oil No. 3), Reindeer moellon, wool grease, and Vac-Grease D. Both worked with raw cod and sulfated cod oils, but the sources were different. Merrill worked with tallow and neatsfoot oil, and Lollar with a second mineral oil.

The results obtained are given in Table I, II, and III.

From these results we conclude:

1. A heating period of 60 to 90 minutes yields a residue weight within 1 per cent of the theoretical with almost all oils, except the partially volatile mineral oils.
2. Again excepting the mineral oils, there seems to be no advantage in using the vacuum oven at 80 - 82°, compared to the forced draft or still air oven at 100 - 105° C.
3. The difference between the residue weight and the theoretical weight is increased by heating for 90 minutes, compared to 60 minutes, at least as often as it is decreased. However, the change in residue weight between 60 and 90 minutes' heating is trivial in most cases (again excepting volatile oils).
4. The use of a tannin dish, in place of the Soxhlet flask, for drying the grease residue increases the error due to loss of volatile matter. This is also the case, to a lesser extent, when the residue is dried in a wide-mouth Erlenmeyer flask.
5. We recommend drying in the extraction flask (either Soxhlet or Erlenmeyer) by heating once only for 90 minutes, in an air oven at 100 -

TABLE I

Effect of Drying Time on Residue Weights of Oils and Greases
Precision Forced-draft oven, 100 - 105° C.

SF : Soxhlet Flask
EF : Erlenmeyer Flask
TD : Tannin Dish
Cincin. : Tanners' Council Laboratory
BDE : B. D. Eisendrath Memorial Lab.

Oil	Laboratory	Container	Cumulative Difference from Theoretical Sample Weight (%)			
			30 min.	60 min.	90 min.	120 min.
Mineral Oil	Cincin.	SF	+1.5	−0.2	−0.3	−0.6
(Finish Oil No. 3)	BDE	SF	0.0	−1.3	−1.6	—
	BDE	EF	−1.4	−2.7	−3.4	—
	Cincin.	TD	−2.4	−5.2	−5.9	−8.1
	BDE	TD	−4.9	−8.5	−12.5	—
Reindeer Moellon	Cincin.	SF	+2.5	+0.2	+0.2	0.0
	BDE	SF	+3.1	+0.5	−0.1	—
	BDE	EF	−0.2	−0.4	−0.5	—
	Cincin.	TD	+0.1	−0.3	−0.4	−0.6
	BDE	TD	−0.7	−0.9	−1.1	—
Vac-grease D	Cincin.	SF	+1.8	+0.2	+0.1	−0.1
	BDE	SF	−0.5	−0.5	−0.8	—
	BDE	EF	−0.1	−0.5	−0.6	—
	Cincin.	TD	0.0	−0.2	−0.5	−0.7
	BDE	TD	−0.6	−0.8	−1.1	—
Wool Grease	Cincin.	SF	+4.6	+1.6	+0.8	+0.5
	BDE	SF	+1.7	+0.8	+0.7	—
	BDE	EF	+0.5	+0.4	+0.5	—
	Cincin.	TD	+0.8	+0.7	+0.7	+0.6
	BDE	TD	+0.4	+0.3	+0.2	—
Cod Oil A	BDE	SF	−0.2	−0.1	−0.1	0.0
	BDE	EF	+0.1	+0.4	+0.6	+0.7
	BDE	TD	−0.3	−0.3	−0.1	0.0
Cod Oil B	Cincin.	SF	+4.4	+1.9	+2.2	+2.6
	Cincin.	EF	+1.5	−0.4	+1.3	+1.3
	Cincin.	TD	+1.2	+1.2	+1.8	+1.7
Sulf. Cod Oil A	BDE	SF	+0.8	+0.8	+0.8	—
	BDE	EF	+0.6	+0.4	+0.2	—
	BDE	TD	−0.7	−0.9	−1.1	—
Sulf. Cod Oil B	Cincin.	SF	+1.5	+0.8	+0.9	+1.0
	Cincin.	EF	+1.5	−0.8	+0.8	0.0
	Cincin.	TD	+0.6	−0.5	0.0	−0.5
Mineral Oil	Cincin.	SF	+3.5	0.0	−0.3	−0.2
125/135 Saybolt Viscosity	Cincin.	EF	−0.9	−3.3	−4.8	−5.3
	Cincin.	TD	−2.5	−3.6	−4.6	−5.1
Tallow	BDE	SF	+0.3	+0.1	−0.2	−0.4
	BDE	EF	+0.3	−0.2	−0.5	−0.7
	BDE	TD	−0.6	−0.9	−1.1	−1.2
Neatsfoot Oil	BDE	SF	+0.4	+0.4	+0.5	+0.7
20° Cloud Test	BDE	EF	+0.6	+0.8	+1.1	+1.5
	BDE	TD	+1.0	+1.1	+1.3	+1.7

105° C., or in a vacuum oven at 80 - 82° C., after first removing the solvent by evaporation at room temperature or by heating on a water bath until the odor of chloroform can no longer be detected. Use of the vacuum oven is essential for accurate results if partially volatile oils are present.

TABLE II

Effect of Drying Time on Residue Weights of Oils and Greases
Still air oven at 100 – 105° C.

SF: Soxhlet Flask
EF: Erlenmeyer Flask
TD: Tannin Dish

Cincin.: Tanners' Council Laboratory
BDE : B. D. Eisendrath Memorial Lab.

Oil	Laboratory	Container	Cumulative Difference from Theoretical Sample Weight (%)			
			30 min.	60 min.	90 min.	120 min.
Mineral Oil	Cincin.	SF	+1.1	+0.6	+0.1	+0.2
(Finish Oil No. 3)	Cincin.	TD	−1.7	−2.3	−3.1	−3.7
Reindeer Moellon	Cincin.	SF	+2.5	+0.8	+0.4	+0.3
	Cincin.	TD	+0.5	+0.4	+0.3	+0.3
Vac grease D	Cincin.	SF	+1.5	+0.4	+0.2	−0.1
	Cincin.	TD	+0.1	0.0	0.0	−0.1
Wool grease	Cincin.	SF	+3.5	+1.0	+0.9	+0.8
	Cincin.	TD	+0.8	+0.8	+0.7	+0.7
Cod Oil B	Cincin.	SF	+8.9	+2.6	+1.1	+2.0
	Cincin.	EF	+7.8	+0.4	−2.3	−1.9
	Cincin.	TD	+1.4	+1.9	+1.8	+2.5
Sulf. Cod Oil B.	Cincin.	SF	+16.5	+3.2	+0.5	+0.5
	Cincin.	EF	−0.4	−2.8	−4.8	−4.8
	Cincin.	TD	+5.0	+0.5	+0.1	+0.5
Mineral Oil	Cincin.	SF	+15.3	+1.3	−0.7	−0.9
125/135 Saybolt Viscosity	Cincin.	EF	−0.6	−3.3	−4.8	−5.3
	Cincin.	TD	+1.5	−1.1	−1.5	−1.6
Neatsfoot Oil	BDE	SF	+0.9	+1.0	+1.0	—
20° Cloud Test	BDE	EF	+0.7	+0.9	+1.3	—
	BDE	TD	+0.3	+0.5	+0.5	—
Tallow	BDE	SF	+1.9	+0.6	+0.6	—
	BDE	EF	−0.9	−1.2	−1.7	—
	BDE	TD	−0.3	−0.6	−1.2	—

Recommended Revised Procedure

We recommend the adoption of the following as a provisional method, to replace the present official method for Petroleum Ether Extract in Vegetable Tanned Leather (B-4) and in Chrome Tanned Leather (D-1).

Matter Extractable by Chloroform

1. *Scope*:—This method is applicable to all types of leather. The material extracted consists predominantly of fats, oils and waxes. Dyes, resins, and certain synthetic tannins, if present, are extracted to a slight extent.

2. *Apparatus*:—Either of the following may be used:

a. The apparatus prescribed by Fed. Specif. KK-L-311, Method 6031 (1950) (practically identical with A. S. T. M. Designation D-231 for examination of knit goods for grease) consisting of:

1. A 400 ml. wide-mouth Erlenmeyer flask, weighing about 60 g.
2. Pyrex siphon cup.
3. Block tin spiral condenser.

TABLE III

Effect of Drying Time on Residue Weights of Oils and Greases
Vacuum Oven at 80-82° C.

SF: Soxhlet Flask
EF: Erlenmeyer Flask
TD: Tannin Dish

Cincin: Tanners' Council Laboratory
BDE: B. D. Eisendrath Memorial Lab.

Oil	Laboratory	Container	Cumulative Difference from Theoretical Sample Weight (%)			
			30 min.	60 min.	90 min.	120 min.
Mineral Oil	Cincin.	SF	+1.5	0.0	0.0	0.0
(No. 3 Finish Oil)	Cincin.	TD	0.0	0.0	−0.3	−0.6
Reindeer Moellon	Cincin.	SF	+2.5	+0.5	+0.4	+0.7
	Cincin.	TD	+0.5	+0.7	+0.5	+0.7
Vac grease D	Cincin.	SF	0.0	−0.2	−0.5	−0.7
	Cincin.	TD	+1.6	+0.7	+0.2	+0.2
Wool grease	Cincin.	SF	+4.0	+1.5	+1.2	+1.2
	Cincin.	TD	+1.0	+1.0	+0.9	+1.0
Cod Oil B	Cincin.	SF	+2.7	+2.1	+1.9	+1.9
	Cincin.	EF	+1.6	+1.1	+1.3	+0.9
	Cincin.	TD	+2.2	+2.3	+2.1	+2.0
Suld. Cod Oil B	Cincin.	SF	+1.7	+1.7	+1.5	+1.4
	Cincin.	EF	+1.0	+0.6	+1.0	+0.8
	Cincin.	TD	+1.6	+1.5	+1.6	+1.4
Mineral Oil	Cincin.	SF	−0.6	−0.4	−0.7	−0.8
(125/135 Saybolt	Cincin.	EF	−1.8	−1.8	−1.7	−2.0
viscosity)	Cincin.	TD	−1.3	−1.3	−1.5	−1.7

4. Metal sample tube, 62 mm. long, whose outside diameter is 1 mm. less than the inside diameter of the siphon cup, with 100 mesh bottom screen. The tube has an indentation 10 mm. long up the side from the bottom to prevent liquid seal. See figure —.

b. All-glass Soxhlet apparatus, consisting of boiling flask, extractor, and condenser, with fat-free cellulose extraction thimbles.
Apparatus *a* is cheaper and permits more rapid extraction than *b*.
Apparatus *b* is better adapted to a large sample.

c. With either *a* or *b* there is required:

1. Electric hot plate, capable of regulation to give the prescribed boiling rate.

2. Drying oven.
3. Desiccator with sulfuric acid, Drierite, anhydrous Al_2O_3, or other efficient desiccant.
4. Analytical balance.
5. Chloroform, U. S. P. or A. C. S. Reagent Grade, not over 1 mg. non-volatile residue per 100 ml. A blank test shall be run on each batch.
6. Fat-free absorbent cotton. The cotton shall be extracted with chloroform before use, or absence of fat proved by analytical extraction of a sample from each package.
7. Glass measuring cylinder.

3. *Sample*:—The sample weight shall be such that the weight of chloroform-soluble material shall be not more than 1 g. nor less than 0.1 g. This means not over 3.0 g. sample weight for a leather containing 30 per cent grease and not less than 5.0 g. for a leather containing 2 per cent grease. The sample shall be prepared as described under B-1 or D-1.

4. *Procedure*:—Weigh the sample (to 1 mg.) into the metal extraction tube (app. 2*a*) with plugs of fat-free absorbent cotton above and below the leather, or into the extraction thimble (app. 2*b*), with a plug of cotton above the leather.

Dry the extraction flask (either apparatus) for 1 hour in the oven at 100 - 105° C., cool 30 minutes in a desiccator, and weigh.

Measure 90 ml. of chloroform into the extraction flask (app. 2*a*) or an amount (app. 2*b*) that will fill the extraction chamber to the siphoning level, leaving 25 to 50 ml. in the flask.

Assemble the apparatus on the hot plate, and pass cold tap water through the condenser. Regulate the heat so that the condensed chloroform siphons back into the flask about every 2 mintes (app. 2*a*) or every 15 minutes (app. 2 *b*). Continue the extraction for 2 hours (app. 2 *a*) or at least 5 hours (app. 2 *b*).

Dissassemble the apparatus. If desired, the bulk of the chloroform may be recovered by connecting the flask to a condenser, placing the flask on the hot plate, and distilling off the bulk of the chloroform. Do not let the flask go dry.

Remove the remainder of the chloroform by spontaneous evaporation at room temperature or by heating the flask on a hot water bath until the odor of chloroform can no longer be detected. The process may be hastened by inserting a tube into the mouth of the flask and applying suction, or a gentle air stream, as convenient.

Place the flask in an oven at 100 - 105°C. for 90 minutes, cool in a desiccator, and weigh.

5. *Calculations*:—Calculate matter soluble in chloroform as percentage of the leather, to 0.1 per cent.

$$\text{Per cent matter sol. in } CHCl_3 = \frac{\text{g. residue X 100}}{\text{g. sample}}$$

6. *Notes*:—

a. If a 15 g. sample must be degreased before determining water solubles, this is best done on a separate sample using apparatus 2 *b*, as the residue weight from a 15 g. sample is excessive for quantitative determination of fat in heavily greased leathers.

b. The practice of reheating the residue, in an attempt to reach approximately constant weight, is not recommended, because of the partial volatility of many oils used in leather, and the tendency of other oils to gain weight, presumably by oxidation.

c. Drying in a vacuum oven at 80° C. is essential for accurate work, if the leather contains partially volatile oil, such as light mineral oil.

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5. For example, U. S. Army Specif. No. 9-97, 18 April 1944, Applicable to vegetable tanned calf leather.
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REPORT OF THE HIDE SUBSTANCE SUB-COMMITTEE

In view of the findings of Dahl and Oehler (J.A.L.C.A. 46, 317-35, 1951), Dr. Merrill, as chairman of the Committee on Pre-Tanning and Post-Tanning Processes, was asked to appoint a sub-committee charged with the cooperative study of their conclusions. Since one of us had initiated the original work which had prompted the studies of Dahl and Oehler, Dr. Merrill appointed him chairman of this sub-committee.

The results of Dahl and Oehler may be summarized as follows:-

(1). Mercury is a more efficient catalyst than copper or selenium. If copper be used, the time of digestion must be prolonged very considerably beyond the time specified by the Official Method if reproducibility and maximum yield of nitrogen are to be obtained. With selenium, on the other hand, long digestion results in loss of nitrogen while short digestion also gives low values and the time factor seems to be very critical.

(2). The amount of boric acid, used to absorb the liberated ammonia, should be as low as is consistent with complete retention of the ammonia as the end-point is sharper the lower the concentration of boric acid.

(3). The smaller the leather sample, the less boric acid is needed and the quicker can the digestion be completed. Samples of re-ground leather (Wiley mill with 4 mm. screen) weighing 0.5 g. gave good agreement between duplicates.

(4). A mixed indicator (e. g. methyl red-methylene blue) gives a sharper end-point than the methyl orange specified in the Official Method.

In order to test these findings thoroughly, it was decided to have four laboratories analyze four leathers in quadruplicate by four methods on four different days. The laboratories were:-

The Leather Section, National Bureau of Standards.
B. D. Eisendrath Memorial Laboratory.
Tanners' Council Research Laboratory.
Howes Leather Company, Inc., Laboratory.

The four leathers chosen were:-

(a) Chrome tanned upper leather, containing 36.5 per cent grease.
(b) Chrome tanned calf leather containing 3 per cent grease.
(c) Vegetable tanned sole leather, containing 5.5 per cent grease.
(d) Vegetable tanned black harness leather, containing 22.2 per cent grease.

The four methods used were:-

(I) The Official Method, exactly as printed, using copper sulfate as catalyst, boric acid absorption and methyl orange indicator.

(II) A modification of the Official Method using copper sulfate, the longer digestion time and the mixed indicator suggested by the work of Dahl and Oehler.

(III) Dahl and Oehler's proposed method. (0.5 g. sample, HgO as catalyst and mixed indicator.

(IV) The same as III but using a 1.4 g. sample, with such changes in time of digestion and quantities of reagent as were thereby made necessary.

In methods III and IV, the Willits-John trap, or the substitute proposed by Dahl and Oehler, was used. For the other methods, the type of trap was optional.

A resume of the several methods is given in Table I.

All samples were prepared by re-grinding through the Wiley Mill with 4 mm. screen, weighed off on filter-paper and sent out by the Bureau of Standards, thereby minimizing errors due to changes in moisture content, different balances and weights, etc. Blank determinations were made on the filter-paper.

TABLE I

Method	I Official ALCA	II Modified ALCA	III Dahl-Oehler	IV Modified Dahl-Oehler
Wt. of sample—grams	1.4	1.4	0.5	1.4
Grams Na_2SO_4	10.0	10.0	7.5*	9.3**
ml. conc. H_2SO_4***	30	30	25	30
Catalyst	$CuSO_4$	$CuSO_4$	HgO	HgO
Grams Catalyst	1.0	1.0	0.5*	0.7**
Digestion Time****	10 min. after clearing.	2 hrs. after clearing.	1¼ hrs Total	1¼ hrs. Total
Treatment after digestion	None	None	$Na_2S_2O_3$	$Na_2S_2O_3$
Boric Acid ml 4% Solution	125	125	50	125
Strength of Acid for Titration	0.3 *N*	0.3 *N*	0.12 *N*	0.3 *N*
Indicator	methyl orange	methyl red — methylene blue		

* 8 g. of a mixture of 100 g. Na_2SO_4 and 7 g. yellow HgO.

** 10 g. of a mixture of 100 g. Na_2SO_4 and 7 g. yellow HgO.

*** 5 ml acid were consumed by the filter paper alone (Whatman No. 41, 11 cm. diameter) and is included in the amounts shown.

****These digestion times were increased by 15 mins. over those required by leather samples alone, to compensate for the delay in clearing due to the filter paper.

The whole experiment was designed to permit statistical analysis of the results. For this reason, each laboratory was instructed to use the same six places on its digestion and distillation equipment and to number these from 1 - 6. Four sets of six Kjeldahl flasks each were used by each laboratory. Each set of six flasks constituted a "rack" and each flask was marked with its "rack" number and position. Thus each flask was used in the same position on both the digestion and distillation apparatus each time it was used and each "rack" was used in the same order each day. Four "racks" were run each day, for four days, each "rack" by a different method each day. Since rotation of blanks and leathers among all six positions would have made the experimental design unduly complicated, the blank runs on the filter paper occupied positions 5 and 6 in all "racks" and the leather samples were rotated among positions 1 - 4. Each "rack", therefore, comprised one sample of each of the 4 leathers plus two blanks on the filter-paper and was analyzed by one of the four methods. All four methods were used each day and, each day, the order of methods was rotated. Each laboratory had a different order of methods and of arrangement of samples within "racks". It will be clear, then, that each leather occupied all four digestion and distillation positions for each method in each laboratory at some time during the test; further, no two laboratories analyzed the same "rack" by the same method at the same time.

TABLE II

Method	Lab	Day	Rack	Blank Corrn. Applied (ml.) Titrant).	LEATHERS Results as % Hide Substance			
					a	b	c	d
I	A	1	1	-0.45	42.13(1)	71.44(2)	29.57(3)	39.02(4)
		2	4	-0.30	41.89(2)	71.6*(1)	29.24(4)	38.53(3)
		3	3	-0.25	41.41(3)	71.82(4)	29.16(1)	37.87(2)
		4	2	-0.20	41.63(4)	72.51(3)	29.29(2)	38.64(1)
I	B	1	4	-0.10	42.16(2)	73.13(1)	29.73(4)	38.77(3)
		2	1	-0.10	42.04(1)	73.10(2)	29.63(3)	38.83(4)
		3	2	-0.17	42.38(4)	73.17(3)	29.57(2)	38.77(1)
		4	3	-0.17	42.37(3)	73.40(4)	29.83(1)	38.96(2)
I	C	1	3	-0.05	42.48(3)	72.59(4)	29.90(1)	38.78(2)
		2	2	-0.30	37.16(4)	72.22(3)	29.28(2)	38.48(1)
		3	1	-0.35	41.84(1)	72.47(2)	29.37(3)	38.40(4)
		4	4	-0.25	42.35(2)	73.08(1)	29.52(4)	38.54(3)
I	D	1	2	-0.21	42.49(4)	72.12(3)	29.78(2)	39.10(1)
		2	3	-0.10	41.81(3)	72.30(4)	30.02(1)	38.71(2)
		3	4	-0.07	42.05(2)	73.08(1)	30.17(4)	37.59(3)
		4	1	0.09	42.25(1)	72.32(2)	29.76(3)	38.83(4)
II	A	1	3	0.00	42.43(2)	73.29(1)	29.82(4)	39.00(3)
		2	2	0.00	42.23(1)	73.55(2)	29.71(3)	38.66(4)
		3	1	0.00	42.49(4)	73.24(3)	29.67(2)	38.95(1)
		4	4	0.00	42.24(3)	72.93(4)	29.61(1)	38.26(2)
II	B	1	2	+0.28	42.75(1)	74.08(2)	30.16(3)	39.38(4)
		2	3	+0.18	42.46(2)	73.59(1)	30.24(4)	38.53(3)
		3	4	+0.23	42.78(3)	74.23(4)	30.31(1)	39.45(2)
		4	1	+0.20	42.68(4)	73.68(3)	29.87(2)	39.25(1)
II	C	1	1	+0.13	42.67(4)	73.91(3)	29.96(2)	39.31(1)
		2	4	+0.10	42.06(3)	73.95(4)	30.53(1)	38.64(2)
		3	3	+0.08	42.86(2)	74.31(1)	30.21(4)	39.14(3)
		4	2	+0.08	42.84(1)	73.94(2)	30.17(3)	39.49(4)
II	D	1	4	+0.12	42.99(3)	72.64(4)	30.17(1)	39.50(2)
		2	1	+0.05	42.32(4)	73.22(3)	30.25(2)	39.51(1)
		3	2	+0.05	37.31(1)	74.05(2)	30.12(3)	39.35(4)
		4	3	+0.05	42.52(2)	73.59(1)	30.20(4)	39.36(3)
III	A	1	2	-0.30	41.98(3)	73.54(4)	29.66(1)	38.67(2)
		2	3	-0.25	42.25(4)	73.38(3)	29.90(2)	39.49(1)
		3	4	-0.25	42.26(1)	72.47(2)	29.81(3)	39.29(4)
		4	1	-0.25	41.74(2)	73.35(1)	30.12(4)	39.11(3)
III	B	1	3	-0.10	43.14(4)	74.29(3)	30.44(2)	39.28(1)
		2	2	-0.05	43.31(3)	74.30(4)	30.17(1)	39.51(2)
		3	1	-0.05	42.69(2)	73.81(1)	30.11(4)	39.29(3)
		4	4	-0.10	42.88(1)	74.06(2)	30.27(3)	39.08(4)
III	C	1	4	-0.15	42.36(1)	74.47(2)	30.25(3)	39.05(4)
		2	1	-0.20	42.87(2)	73.49(1)	30.43(4)	39.34(3)
		3	2	-0.20	42.66(3)	73.88(4)	30.31(1)	38.93(2)
		4	3	-0.20	42.47(4)	73.46(3)	30.24(2)	39.09(1)
III	D	1	1	-0.16	42.26(2)	73.63(1)	29.56(4)	38.93(3)
		2	4	-0.10	42.26(1)	72.54(2)	30.32(3)	38.93(4)
		3	3	-0.15	42.31(4)	72.75(3)	30.01(2)	38.62(1)
		4	2	0.00	42.72(3)	73.37(4)	30.43(1)	39.10(2)
IV	A	1	4	0.00	42.14(4)	73.56(3)	29.82(2)	39.12(1)
		2	1	0.00	42.45(3)	73.11(4)	29.82(1)	38.38(2)
		3	2	0.00	42.52(2)	72.96(1)	29.56(4)	38.80(3)
		4	3	0.00	42.63(1)	71.77(2)	30.48(3)	38.78(4)
IV	B	1	1	+0.23	42.98(3)	73.93(4)	30.16(1)	39.53(2)
		2	4	+0.20	43.27(4)	74.19(3)	30.34(2)	39.54(1)
		3	3	+0.20	42.95(1)	73.95(2)	30.46(3)	39.35(4)
		4	2	+0.18	43.30(2)	74.17(1)	30.21(4)	39.51(3)
IV	C	1	2	+0.10	43.24(2)	73.98(1)	30.12(4)	39.56(3)
		2	3	+0.10	42.78(1)	73.21(2)	29.90(3)	38.85(4)
		3	4	+0.08	42.95(4)	74.06(3)	30.40(2)	39.62(1)
		4	1	+0.07	42.90(3)	74.31(4)	30.08(1)	39.50(2)
IV	D	1	3	+0.09	42.90(1)	73.59(2)	30.27(3)	39.53(4)
		2	2	-0.05	42.28(2)	72.38(1)	30.30(4)	39.24(3)
		3	1	-0.01	37.25(3)	73.60(4)	30.10(1)	39.28(2)
		4	4	-0.06	42.73(4)	73.92(3)	30.39(2)	39.41(1)

NOTE:-Numbers in parentheses designate position number of flask and burner in each rack.

All laboratories completed the work and sent their corrected buret readings to the Bureau of Standards for conversion to percent Hide Substance, and for statistical analysis of the results.

The data obtained by each laboratory are shown in Table II.

Perusal of this table will immediately show that leather "a" caused the most trouble and that, on this same leather, Lab. C had one and Lab. D had two very erratic results. The reasons for these erratic results are not known but their similarity suggests some recurrent error. Omitting these three figures, a preliminary breakdown of the results is given in Table III:-

From Table III, the following conclusions have been drawn:-

(1). In all cases, the Official Method gave lower results than did the other three methods. The difference is about 0.5 per cent hide substance for leathers *a*, *c* and *d*, and 1 per cent for leather *b*. This was further confirmed by two of the cooperating laboratories (A and D), using their own routine leather samples.

(2). There is no significant difference between the results obtained by methods II, III or IV.

(3). Considering only methods II, III and IV, there is no significant difference in concordance between laboratories. Whether the maximum difference between laboratory averages or the average deviation of individual laboratory averages from the grand average be taken as the criterion, it will be seen that concordance on leather *a* and *b* was best by method II; on leather *d*, by method III; on leather *c*, by method IV. If methods III and IV, which differed only in size of sample, be considered, it will be seen that method III gave best concordance on leather *d*; method IV on leather *a*; no appreciable difference on leathers *b* and *c*. Apparently, on reground leather, just as good agreement can be obtained with a 0.5 g. sample as with a 1.4 g. sample. The necessity for regrinding, when only 0.5 g. leather is used, was checked by Mr. Dahl and the results, given in Appendix I to this report, show that regrinding is necessary for some leathers at least.

(4). Concerning inter-laboratory agreement, Laboratory A was consistently lower than B and C, while Laboratory D, in general, obtained results between A and B/C, with some figures as low as, or lower than, A and some as high as, or higher than, B/C. No reason has yet been discovered for these differences but it should be noted that A and D used electrical heating for digestion whereas B and C used gas. An attempt to check this was made by Mr. Ellison and his results are given in Appendix II. From those data, it would seem that electric versus gas heating is probably not a major factor.

If, instead of grand averages, results obtained for a given pair of duplicates (from Table II) be considered, it will be evident that none of the methods gives truly satisfactory inter-laboratory agreement.

TABLE III

METHOD	LAB.	LEATHER *a* Chrome Upper			LEATHER *b* Chrome Calf			LEATHER *c* Vegetable Sole			LEATHER *d* Vegetable Harness		
		Mean of 4 detns.	Max. diff. (1)	Av. deviation. (2)	Mean of 4 detns.	Max. diff.	Av. deviations.	Mean of 4 detns.	Max. diff.	Av. deviation.	Mean of 4 detns.	Max. diff.	Av. deviation
I	A	41.8	0.7	0.25	71.9	1.1	0.4	29.3	0.4	0.2	38.5	1.15	0.25
	B	42.2	0.3	0.1	73.2	0.3	0.1	29.7	0.3	0.1	38.8	0.2	0.1
A.L.C.A.	C	42.2*	0.6	0.3	72.6	0.9	0.25	29.5	0.6	0.2	38.55	0.4	0.1
	D	42.15	0.7	0.2	72.5	1.0	0.3	29.9	0.4	0.2	38.6	1.5	0.5
II	A	42.35	0.3	0.1	73.25	0.6	0.2	29.7	0.2	0.1	38.7	0.7	0.3
Modified	B	42.7	0.3	0.1	73.9	0.6	0.3	30.15	0.4	0.1	39.15	0.9	0.3
A.L.C.A.	C	42.6	0.8	0.3	74.0	0.4	0.1	30.2	0.5	0.2	39.15	0.85	0.3
	D	42.6*	0.7	0.2	73.4	1.4	0.45	30.2	0.1	0.04	39.4	0.2	0.1
III	A	42.1	0.5	0.2	73.4	1.1	0.4	29.9	0.5	0.1	39.1	0.4	0.25
Dahl-	B	43.0	0.6	0.2	74.2	0.5	0.2	30.25	0.3	0.1	39.3	0.4	0.1
Oehler	C	42.6	0.5	0.2	73.7	1.0	0.35	30.3	0.2	0.1	39.1	0.4	0.1
	D	42.4	0.5	0.2	73.0	1.1	0.4	30.1	0.9	0.3	38.9	0.5	0.15
IV	A	42.4	0.5	0.15	72.85	1.9	0.5	29.9	0.9	0.3	38.8	0.7	0.2
Modified	B	43.1	0.35	0.2	74.1	0.3	0.1	30.3	0.3	0.1	39.5	0.2	0.1
Dahl-	C	43.0	0.5	0.1	73.9	1.1	0.3	30.1	0.5	0.1	39.4	0.8	0.3
Oehler	D	42.6*	0.6	0.2	73.4	1.5	0.5	30.3	0.3	0.1	39.4	0.3	0.1

*One erratic determination was disregarded.

		Means for 4 labs.	Max. diff. (3)	Av. deviation (4)	Mean for 4 labs.	Max. diff.	Av. deviation	Mean for 4 labs.	Max. diff.	Av. deviation	Mean for 4 labs.	Max. diff.	Av. deviation
I	All	42.1	0.5	0.2	72.5	1.4	0.4	29.6	0.6	0.2	38.6	0.3	0.1
II	All	42.6	0.3	0.1	73.6	0.8	0.3	30.1	0.5	0.2	39.1	0.7	0.2
III	All	42.5	0.95	0.3	73.55	1.05	0.4	30.1	0.4	0.15	39.1	0.4	0.1
IV	All	42.6	0.7	0.3	73.55	1.2	0.4	30.15	0.4	0.1	39.25	0.7	0.2

(1) Spread between high and low determinations.
(2) Av. difference of individual determinations from mean.
(3) Spread between averages of highest and lowest laboratory.
(4) Av. difference between individual labs and av. for all labs.

A statistical study of the data was made by Messrs. Dahl and Mandel, and their co-workers, of the Bureau of Standards and their report is given in Appendix III, from which it will be seen that the statistical study confirms the conclusions reached above.

The following miscellaneous information and comments were received from the cooperating laboratories:-

Laboratory A.

Standardization of acid against acid potassium phthalate. Standardization figures rechecked with own primary standard sample (Merck's ACS primary standard) as well as against the acid potassium phthalate used by Laboratory B (Bureau of Standards certified acid potassium phthalate primary standard). Rechecks did not alter original values to any significant degree. Had breakage of two flasks during distillation, both with Method IV, not the same racks. The two racks were re-run.

Used Willitt-John traps for all methods.

Likes speed of the mercuric oxide method and likes the mixed indicator. Thinks perhaps a smaller quantity of indicator is preferable. Thinks the Willits-John trap an improvement over the old type.

Clearing time was 30 to 40 minutes with $CuSO_4$ (Methods I and II) and much less (15 to 20 minutes) with HgO (Methods III and IV). Surprised at the much longer clearing time reported by Laboratory C (See below).

Laboratory B.

Standardization against acid potassium phthalate (Bureau of Standards certified sample). Rechecked standardization values both against acid potassium phthalate and sodium carbonate without finding any significant difference. (Laboratories A and B, having the lowest and highest results, respectively, made this recheck in order to determine if the disagreement might be due to standardization differences, which apparently is not the case).

Noted sputtering and foaming at the initial period of digestion with leathers *a* (especially) and *b*.

Found it difficult to define "clearing time", especially with chrome leathers.

Prefers Method III because:

(1). Smaller samples are more easily digested (shorter time), less sputtering and foaming, less conc. sulfuric acid required during digestion.

(2). This results in less tendency to bump during distillation, as less alkali is required to neutralize the acid and the mixture is therefore less concentrated in sodium sulfate (which has a marked tendency to increase bumping).

(3). Permits titration with a lower concentration of boric acid, which increases the sharpness of the end-point and decreases the possibility of error due to unequal dilution of the samples and the blanks.

Used Willits-John traps for all methods.

Laboratory C.

Sputtering and foaming of the two chrome leathers with methods III and IV in the initial period of digestion. Worse with method IV than with III. Methods I and II were started at low heat for about 10 minutes and no sputtering or foaming were noted with these.

Acids standardized against sodium carbonate.

Willits-John traps used for all methods.

Average clearing times (minutes) were:-

Leathers	*a*	*b*	*c*	*d*	Blank
METHODS					
I	68	62	56	61	40
II	69	65	58	57	38
III	41	39	35	39	32
IV	49	40	47	47	29

Laboratory D.

Standardization of solutions	Alkali	Acid
Base: against benzoic acid (NBC 39f)	0.2434	0.3056
against acid potassium phthalate, Eastman Kodak 538	0.2418	0.3034
Acid: against tris(hydroxymethyl) amino-methane (G. F. Smith)		0.3057
sodium carbonate (boiling solution bromthymol blue indicator)		0.3055

Normality used 0.3055

(There is good agreement between all except the acid potassium phthalate values).

Tris(hydroxymethyl)amino methane is an amino-compound whose amino group can be titrated, directly, with standard acid, and this compound was titrated both directly and also after being subjected to the Kjeldahl procedure. The efficiency figures reported are the percentage which the latter titration is of the first. (titration expressed as ml. of reagent per g. of compound).

Method:	I	II	III	IV
No. of Determinations	2	12	2	10
Efficiency Mean of Determinations	92.75	98.58	98.87	99.12
Standard Deviation	0.08	0.95	0.18	0.72
Coefficient of Variation		0.96		0.73

(This clearly shows the low efficiency of Method I).

Dislikes the use of steel-wool plugs instead of the Willits-John traps because difficerence in tightness of plug might produce variability in scrubbing action. Willis-John traps are satisfactory. However, if 220 mesh carborundum is used (instead of zinc) to prevent bumping during distillation, no alkali carry-over occurs even with the old type Kjeldahl traps. Laboratory D has used this method for years and has never noticed any measurable carry-over of alkali. Used the Willits-John traps for Method III and the steel wool traps for Method IV. Ordinary cylindrical traps were used for Methods I and II. Carborundum was used as the antibump throughout this work.

Laboratory D feels certain that the so-called "blanks" are really indicator errors.

All titrations were done with the Fisher titrimeter to supplement the indicator. Could not have used Method I without it. The endpoint with methyl orange indicator varies over a whole pH unit (pH 4.5 - 3.5). The mixed indicator's endpoint was consistently between pH 5.05 and 4.90. The two abnormal values (about 5 per cent too low) were noted to be probably abnormal by the analyst. One gave a cloudy distillate. It was run by Method IV using the steel-wool plug. (The cloudy distillate was noted on several samples run by method IV). The other abnormal sample (run by Method II) had to be back-titrated, as the endpoint was overrun, but there was no other reason to suspect the result. Has noted such abnormal results before, with Army retan leathers high in grease.

Recommendations

On the basis of the above, it is our unanimous recommendation that the following changes be made in the Official A.L.C.A. method for the determination of nitrogen in leather:-

(1). If copper sulfate be used as catalyst, 2 hours' digestion, after clearing, shall be required.

(2). Permit the use of yellow mercuric oxide as catalyst.

(3). Eliminate the permissible use of selenium as catalyst. Please note that this recommendation is not based upon the work of this committee but upon the work of Dahl and Oehler (loc. cit.) which confirms the findings of others, notably: Patel and Sreenavasar, *Anal. Chem.* **20**, 63-5, (1948); and Bradstreet, *Anal. Chem.* **21**, 1012-3, (1949).

(4). Require the use of a mixed indicator (methyl red-methylene blue) instead of the methyl orange now specified.

(5). Permit use of a 0.5 g. sample, if the leather be reground.

(6). If any, or all, of the above be approved, rewrite the whole method, making the necessary minor changes in quantities of reagent.

The Committee regards Recommendations (1) and (4) as essential and urgent.

(7). Despite the better concordance obtained by Methods II, III and IV, the committee considers the inter-laboratory differences to be too great and suggests that the Bureau of Standards be asked to continue their research on this problem. This is not to be construed as implying criticism of the earlier work carried out by the Bureau of Standards (Dahl & Oehler, loc. cit.). On the contrary, without the very detailed information obtained from that work, and lacking the tremendous amount of help which the Bureau provided in laying out the test, preparing the samples and evaluating the results, the present study could not have been made. The other members of this committee are unanimous in this regard.

Acknowledgments

The committee wishes to thank Messrs. E. L. Wallace, R. B. Hobbs, Rene Oehler and J. Mandel (statistician) of the National Bureau of Standards, for all they have done to make this study possible. The chairman would also like to thank the cooperating members for their efforts, comments and criticism which have gone into the compiling of this report. He is also indebted to Messrs. C. A. Blair, F. O'Flaherty, F. F. Marshall, R. L. Moore, J. S. Rogers, E. L. Wallace and L. M. Whitmore who cooperated so keenly in the earlier work which led to the present studies.

Respectfully submitted:-

H. B. Merrill, (Chairman of Committee on Pre-tanning & Post-tanning Processes)
S. Dahl,
R. M. Lollar,
H. L. Ellison,
A. N. Kay, (Chairman, Hide-Substance Sub-Committee)

Appendix I

In an effort to determine whether or not regrinding of the leather was absolutely necessary when only 0.5 g. portions were to be used for the determination of Hide Substance, the following test was run by Mr. Dahl:-

Preparation I Leather cut in pieces approximately 1 cm. square, mixed, ground (4 mm. screen) and mixed.

Preparation II Leather cut in strips, ground (4 mm. screen), mixed, reground (same screen) and mixed. (This is the type of preparation used in the collaborative work).

Preparation III Leather cut in strips, ground 3 times (2 mm. screen) and mixed after each grinding.

In the Table below, are the results obtained given as standard deviations in percentage of Hide Substance. These standard deviations are, in each case, calculated from 4 replicates run simultaneously by Method III.

Leather	Preparation I	Preparation II	Preparation III
a*	0.69; 0.46; 0.66	0.41; 0.24; 0.53	0.17; 0.19; 0.17
b*	0.57; 0.32	0.16; 0.32	
c*	0.14; 0.14	0.19; 0.15	

*LEATHER

a. Chrome tanned upper, same as *a* in collaborative work.
b. Army Retan Leather.
c. Vegetable Sole Leather, same as *c* in collaborative work

These results clearly indicate that regrinding gives improved concordance for some leathers, at least, and that grinding several times through a smaller screen might be the best preparation.

Appendix II.

In order to check the possibility that electric versus gas heating might be a significant factor, as suggested in Point (4) of the report, Dr. Merrill and Mr. Ellison ran the following tests:-

Using the special Kjeldahl flasks with thermometer well which were used by Dahl and Oehler (loc. cit.) and using 25 ml. sulfuric acid and one digestion tablet, containing 10 g. sodium sulfate and 0.65 g. anhydrous copper sulfate, in each case, the following results were obtained:-

Heat	Temp. °C.	Remarks
ELECTRIC		
High**	341	No leather
High**	346	0.8 g. Leather
Low*	336	No Leather
GAS*	335	No Leather

*Regulated so that acid condensed just inside lower end of neck of Kjeldahl flask.
**Acid condensed half-way up neck of flask.

From the above, it appears that electric and gas heats give the same temperature under like conditions. If the heat be increased, so that more of the acid is in the condensed film or in the vapor phase, the temperature of the mixture will be higher, as might be expected.

To check the effect of type of heating on the actual hide substance, 3 leathers were run, in quadruplicate, all with electric heat for digestion—2 samples of each leather with the heat regulated so that the acid condensed at the lower end of the neck, and 2 samples of each at full heat so that the acid condensed about half-way up the neck. Expressed as percent hide substance, the following results were obtained:-

	REDUCED HEAT			FULL HEAT		
LEATHER	(1)	(2)	Av.	(1)	(2)	Av.
1	72.3	72.0	72.15	72.2	71.9	72.05
2	73.9	74.3	74.1	74.4	74.5	74.45
3	73.0	72.8	72.9	72.7	72.7	72.7

While these tests do not take into account possible differences in the temperature of the liquid film on the glass walls adjacent to the source of heat, it does not seem as if the difference in method of heating is responsible for the inter-laboratory differences found.

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APPENDIX III.

STATISTICAL STUDY OF THE ANALYTICAL DATA OBTAINED IN THE COLLABORATIVE HIDE SUBSTANCE STUDY.

The data contain three values that differ so greatly from the rest that they probably contain gross errors. However, since no other valid reason exists for rejecting them, this study was made both with these values and without them. The numbers marked by an asterisk in the tables are those obtained when one or more of these values have been excluded in the calculations.

Each laboratory has analyzed one sample of each of four leathers by four different methods each day for four days. The four results for any particular leather, method, and laboratory are replicates, except for variations arising from difference in days, racks, and burner-flask positions.

The means, standard deviations, and coefficients of variation for each group of replicates are given for each laboratory in tables 1, 2, 3, and 4. In all laboratories Method I is found to give significantly lower results than the other methods. (In the case of laboratory D, this is true only when the two abnormal values are excluded.) The burner-flask position number 2 of laboratory A gives significantly lower results* than the other three burners, which do not differ significantly among themselves. Rack number 1 of laboratory B gives lower results than the other racks, which do not differ among themselves.

*Low results were found for this position for other leathers, probably due to a defective trap, as the difference disappeared after another trap was substituted.

TABLE I

Study of Results from Laboratory A.

		Leat ers			
	Method	a	b	c	d
I	Mean % H. S.	41.76	71.85	29.32	38.52
	*Standard dev. % H. S.	0.31	0.46	0.18	0.48
	Coefficient of var.	0.74	0.64	0.61	1.25
II	Mean % H. S.	42.45	73.25	29.70	38.72
	Standard dev. % H. S.	0.13	0.25	0.09	0.34
	Coefficient of var.	0.31	0.34	0.30	0.88
III	Mean % H. S.	42.06	73.19	29.87	39.14
	Standard dev. % H. S.	0.25	0.48	0.19	0.35
	Coefficient of var.	0.59	0.66	0.64	0.89
IV	Mean % H. S.	42.44	72.85	29.92	38.77
	Standard dev. % H. S.	0.21	0.76	0.39	0.30
	Coefficient of var.	0.49	1.04	1.3	0.77

*Standard deviations and Coefficients of variation refer to the precision of a single measurement.

Composite Averages of All Leathers for Each Burner

	Burner-Flask Positions			
Methods	1	2	3	4
I	45.40	45.12	45.51	45.43
II	46.02	45.98	46.05	45.98
III	46.19	45.70	46.07	46.30
IV	46.13	45.62	46.32	45.90
Average	46.01	45.61	45.99	45.90

Conclusions: (1) Method I gives lower results than the other methods.
(2) Burner-flask position 2 gives lower results than the other burners.

The statistical analysis (Table 8) shows that the differences in both methods and burners are significant. Burners 1, 3, and 4 do not differ significantly between themselves.

Table 5 is a comparison of the means from all laboratories, for each leather and method, as well as a comparison among the laboratories for each method of the average of all leathers. The results of Method I are significantly lower than those for the other methods, which do not differ significantly among themselves. There is also a significant difference between laboratories. The results of laboratories B and C are in good agreement, but are higher than those of A and D. (Laboratories A and B have rechecked their standardization of the acids, and the difference between them apparently is not due to this factor.)

TABLE 2

Study of Results from Laboratory B

Method		Leathers a	b	c	d
I	Mean % H. S.	42.28	73.20	29.69	38.83
	Standard dev. % H. S.	0.17	0.14	0.11	0.09
	Coefficient of var.	0.40	0.19	0.37	0.23
II	Mean % H. S.	42.67	73.90	30.15	39.15
	Standard dev. % H. S.	0.14	0.31	0.19	0.42
	Coefficient of var.	0.33	0.42	0.63	1.07
III	Mean % H. S.	43.01	74.12	30.25	39.29
	Standard dev. % H. S.	0.27	0.23	0.14	0.18
	Coefficient of var.	0.63	0.31	0.46	0.46
IV	Mean % H. S.	43.13	74.06	30.29	39.48
	Standard dev. % H.S.	0.19	0.14	0.13	0.09
	Coefficient of var.	0.44	0.19	0.43	0.23

Composite Averages of All Leathers for Each Rack

Method	Racks 1	2	3	4
I	45.90	45.97	46.14	45.95
II	46.37	46.59	46.21	46.69
III	46.48	46.82	46.79	46.57
IV	46.65	46.80	46.68	46.84
Average	46.35	46.55	46.46	46.51

Conclusions: (1) Method I gives lower results than the other methods.
(2) Rack I gives lower results than the other racks.

The statistical analysis (table 9) shows that the differences in both methods and racks are significant.

Racks 2, 3 and 4 do not differ significantly among themselves.

Table 6 is a comparison betwen laboratories for each leather when Method I is excluded. These means represent the most reliable estimates of percentage of hide substance of each leather for each laboratory. The standard error and percentage of standard error of these means are also given to indicate their degree of certainty. (Standard error and percentage of standard error=standard deviation and coefficient of variation, respectively, x $\frac{1}{\sqrt{N}}$ where N is the number of determinations of each mean, in this case 12.) The composite average of all leathers for each laboratory gives the comparison among laboratories based on their most reliable results.

TABLE 3
Study of Results from Laboratory C

Method		Leathers a	b	c	d
I	Mean % H. S.	40.96 *(42.18)	72.59	29.52	38.55
	Standard dev. % H. S.	2.55 (0.34)	0.36	0.27	0.16
	Coefficient of var.	6.23 (0.81)	0.50	0.91	0.42
II	Mean % H.S.	42.61	74.03	30.22	39.15
	Standard dev. % H. S.	0.37	0.19	0.24	0.36
	Coefficient of var.	0.87	0.26	0.79	0.92
III	Mean % H. S.	42.59	73.82	30.31	39.10
	Standard dev. % H. S.	0.22	0.47	0.09	0.17
	Coefficient of var.	0.52	0.64	0.30	0.43
IV	Mean % H. S.	42.97	73.89	30.13	39.38
	Standard dev. % H. S.	0.19	0.47	0.21	0.36
	Coefficient of var.	0.44	0.64	0.70	0.91

*Values obtained when one abnormal result was omitted.

Conclusion: Method I gives lower results than the other methods.

The statistical analysis (table 10) shows that the difference is significant whether the one abnormal value is included in the calculation or not.

TABLE 4
Study of Results from Laboratory D

Method		Leathers a	b	c	d
I	Mean % H. S.	42.15	72.46	29.93	38.56
	Standard dev. % H. S.	0.29	0.43	0.20	0.67
	Coefficient of var.	0.69	0.59	0.67	1.74
II	Mean % H. S.	41.29 *(42.61)	73.38	30.19	39.43
	Standard dev. % H. S.	2.67 (0.36)	0.60	0.05	0.09
	Coefficient of var.	6.45 (0.84)	0.82	0.16	0.23
III	Mean % H. S.	42.39	73.07	30.08	38.89
	Standard dev. % H. S.	0.22	0.51	0.39	0.20
	Coefficient of var.	0.52	0.70	1.30	0.51
IV	Mean % H. S.	41.29 *(42.64)	73.37	30.27	39.37
	Standard dev. % H. S.	2.71 (0.26)	0.68	0.12	0.13
	Coefficient of var.	6.56 (0.61)	0.93	0.40	0.33

*Values obtained when one abnormal result was omitted.

Conclusion: Method I gives lower results than the other methods when the two abnormal values are excluded.

The statistical analysis (table 11) shows that the difference is significant. When the two abnormal results are included there is no difference between methods on the average for all four leathers.

TABLE 5

Mean % Hide Substance Found in Each Leather by Each Method and Laboratory.

Laboratory	A				B				C				D				Composite average of all leathers			
Leather / Method	a	b	c	d	a	b	c	d	a	b	c	d	a	b	c	d	A	B	C	D
I	41.76	71.85	29.32	38.52	42.28	73.20	29.69	38.83	40.96 *(42.96)	72.59	29.52	38.55	42.15	72.46	29.93	38.56	45.36	45.99	45.40 *(45.71)	45.77
II	42.45	73.25	29.70	38.72	42.67	73.90	30.15	39.15	42.61	74.03	30.22	39.15	41.29 *(42.61)	73.38	30.19	39.43	46.01	46.46	46.50	46.07 *(46.40)
III	42.06	73.19	29.87	39.14	43.01	74.12	30.25	39.29	42.59	73.82	30.31	39.10	42.39	73.07	30.08	38.89	46.06	46.66	46.46	46.11
IV	42.44	72.85	29.92	38.77	43.13	74.06	30.29	39.48	42.97	73.89	30.13	39.38	41.29 *(42.64)	73.37	30.27	39.37	45.91	46.74	46.59	46.07 *(46.41)

All values are means of four determinations except * where one abnormal value is excluded in each case.

Conclusions: Method I gives lower results than the other methods. The analysis of variance (table 12) shows that this difference is significant.

Methods II, III, and IV do not differ significantly among themselves.

TABLE 6.

Study of Results (excluding Method I) from All Laboratories.

Laboratory		Leathers a	b	c	d	Composite av. of all leathers
A	Mean % H. S.	42.32	73.10	29.83	38.88	46.03
	Standard error	0.06	0.16	0.07	0.09	
	% standard error	0.14	0.22	0.23	0.23	
B	Mean % H. S.	42.94	74.03	30.23	39.31	46.63
	Standard error	0.06	0.07	0.05	0.08	
	% standard error	0.14	0.09	0.17	0.20	
C	Mean % H. S.	42.72	73.91	30.22	39.21	46.52
	Standard error	0.08	0.12	0.05	0.09	
	% standard error	0.19	0.16	0.17	0.23	
D	Mean % H. S.	41.66	73.27	30.18	39.23	46.08
		*(42.55)				*(46.31)
	Standard error	0.63	0.15	0.09	0.04	
		(0.09)				
	% standard error	1.51	0.20	0.30	0.10	
		(0.21)				

*The two abnormal test results omitted.

Conclusion: The differences found between the laboratories are significant, as shown by analysis of variance (table 12).

Table 7 is a comparison of precision (in standard deviations) for each leather, method, and laboratory. The overall highest precision was obtained with leather *c*, the lowest with leather *b*, when the abnormal values were excluded. These all occurred with leather *a*, which therefore gave the poorest precision when the abnormal values were included in the calculations. The difference in precision among the leathers is significant. There is no significant difference in precision among the methods. These conclusions are valid whether the abnormal values are included or not.

TABLE 7

Standard Deviations in % H. S. for each Method, Leather, and Laboratory.

Leather	a				b				c				d				Average standard deviation for all methods			
Method—Laboratory	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV	a	b	c	d
A	0.31	0.13	0.25	0.21	0.46	0.25	0.48	0.76	0.18	0.09	0.19	0.39	0.48	0.34	0.35	0.30	0.24	0.52	0.24	0.37
B	0.17	0.14	0.27	0.19	0.14	0.31	0.23	0.14	0.11	0.19	0.14	0.13	0.09	0.42	0.18	0.09	0.20	0.21	0.15	0.23
C	2.55 '(0.34)	0.37	0.22	0.19	0.36	0.19	0.47	0.47	0.27	0.24	0.09	0.21	0.16	0.36	0.17	0.36	1.30 *(0.29)	0.39	0.20	0.28
D	0.29	2.67 *(0.36)	0.22	2.71 *(0.36)	0.43	0.60	0.51	0.68	0.20	0.05	0.39	0.12	0.67	0.09	0.20	0.13	1.91 *(0.30)	0.56	0.23	0.36
Average	1.29 *(0.29)	1.35 *(0.27)	0.24	1.37 *(0.23)	0.37	0.37	0.44	0.57	0.20	0.16	0.24	0.24	0.42	0.33	0.24	0.25	1.16 *(0.26)	0.38	0.21	0.32

The standard deviations are calculated from four replicates (and refer to the standard deviation of a single determination) except where * one abnormal value was excluded. The replicates include variations due to burner-flask positions, racks and days.

Conclusion: The analysis of variance of precision (table 13) shows that there is no significant difference in precision among the methods, but that there is a significant difference in precision among the leathers.

TABLE 8

Analysis of Variance

Results from Laboratory A

Source of variance	Degrees of freedom	Sum of squares	Mean squares	Variance Ratio (F)
Total	63	1933123		
Methods	3	52461	17487	11.9 (significant)
(Leathers)	3	1791702		
Days	3	3063	1021	0.7
Racks	3	1037	346	0.2
Burner-flask positions	3	14137	4712	3.2 (significant)
Residual	48	70723	1473	
Breakdown of burner-flask positions, sum of squares:				
Positions 1, 3, 4	2	603	302	0.21
Positions 2 vs 1, 3, 4	1	13534	13534	9.2 (significant)

TABLE 9

Analysis of Variance

Results from Laboratory B

Source of variance	Degrees of freedom	Sum of squares	Mean squares	Variance ratio (F)
Total	63	1987340		
Methods	3	54560	181897	45.8 (significant)
(Leathers)	3	1909105		
Days	3	260	87	
Racks	3	3577	1192	3.0 (significant)
Burner-flask positions	3	832	277	0.7
Residual	48	19006	397	
Breakdown of racks, sum of squares:				
Racks, 2, 3, 4	2	717	358	0.9 (not significant)
Racks 1 vs 2, 3, 4	1	2860	2860	7.2 (significant)

TABLE 10

Analysis of Variance
Results from Laboratory C

Source of variance	Degrees of freedom	Sum of squares	Mean squares	Variance ratio (F)
		All values included.		
Total	63	1990843		
Methods	3	1498732	49958	11.7 (significant)
Leathers	3	1575362		
Days	3	36903	12301	2.9
Racks	3	11234	3745	0.9
Burners	3	12966	4322	1.0
Residual	48	204505	4261	
		One abnormal value excluded.		
Total	63	1974582		
Methods	3	79406	26469	25.6 (significant)
Leathers	3	1835829		
Days	3	7657	2552	2.5
Racks	3	792	264	0.2
Burners	3	1238	313	0.3
Residual	48	49660	1035	

TABLE 11

Analysis of Variance
Results from Laboratory D

Source of variance	Degrees of freedom	Sum of squares	Mean squares	Variance ratio (F)
		All values included.		
Total	63	1778495		
Methods	3	11670	3890	0.3
Leathers	3	1197460		
Days	3	66241	22080	2.3
Racks	3	15901	5300	0.5
Burners	3	17819	5940	0.5
Residual	48	469404	9779	
		Two abnormal values excluded.		
Total	63	1856068		
Methods	3	43397	14466	10.4 (significant)
Leathers	3	1736788		
Days	3	6795	2265	1.6
Racks	3	394	131	0.1
Burners	3	1702	567	0.4
Residual	48	66992	1396	

TABLE 12

Analysis of Variance
Results from all Laboratories

Source of Variance	Degrees of freedom	All values included			Three abnormal values excluded		
		Sum of squares	Mean squares	Variance ratio (F)	Sum of squares	Mean squares	Variance ratio (F)
Total	63	28050242			30747792		
(Leathers)	3	25573577			28931542		
Laboratories	3	546040	182013	12.0 (signif.)	516845	172282	50.5 (signif.)
Methods	3	894104	298035	19.6 (signif.)	597394	199131	58.4 (signif.)
Labs x Methods	9	180154	20017	1.3	71895	7988	2.3
Labs x Leathers	9	320946	35661	2.3	162153	18017	5.3 (signif.)
Leathers x Methods	9	125365	13929	0.9	375896	41766	12.2 (signif.)
Labs x Leathers x Methods	27	410056	15187		92067	3410	
Pooled Error	45		15902			4555	
" "	36						
Breakdown of Methods							
II, III, IV	2	11050	5525	0.4 (not signif.)	17892	8946	1.96 (not signif.)
I vs II, III, IV	1	883054	883054	55.5 (signif.)	579502	579502	1.27 (signif.)

TABLE 13

Analysis of Variance of Log of S^2 (Variance of Precision)

Source of Variance	Degrees of freedom	All values included			Three abnormal values excluded		
		Sum of squares	Mean squares	Variance ratio (F)	Sum of squares	Mean squares	Variance ratio (F)
Total	63	289521			167060		
Methods	3	1717	572	0.1	909	303	0.2
Leathers	3	49145	16382	3.8 (signif.)	36721	12260	9.8 (signif.)
Laboratories	3	34921	11640	2.7	22151	7384	5.9 (signif.)
Methods x Leathers	9	14946	1661	0.4	11237	1248	1.0
Methods x Laboratories	9	25870	2874	0.7	25653	2850	2.3
Leathers x Laboratories	9	45569	5063	1.2	19107	2123	1.7
Methods x Leathers x Laboratories	27	117353	4346		51282	1247	
Pooled error	54		3773			1986	
Breakdown of Leathers, Sum of Squares							
a, b, d	2	12900	6450	1.7 (not signif.)	1252	626	0.3 (not signif.)
c, vs a, b, d	1	36245	36245	9.6 (signif.)	35469	35469	18.0 (signif.)

Summary of Results

1. Method I gives significantly lower results than the other methods. On the average this difference is 0.7 per cent hide substance. There is no significant difference in accuracy or precision among Methods II, III, and IV.
2. There is a significant difference in precision among the four leathers. Excluding the three abnormal values, the standard deviations, in percentage of hide substance, averaged for all methods and laboratories were 0.26, 0.38, 0.21, and 0.32 for the four leathers *a*, *b*, *c*, and *d*. The three abnormally low values all occurred with leather *a*. Including these values, the average standard deviation for leather *a* was 1.16.
3. There is a significant difference between laboratories. The average range (difference between the laboratory with the highest results, B, and that with the lowest results, A) is about 0.6 per cent hide substance. The agreement between laboratories is no better with one method than with another for Methods II, III, and IV.
4. Laboratory A shows a significant difference in burner-flask positions. The average result for position number 2 is about 0.4 per cent (hide substance) lower than the average of the other positions.
5. Laboratory B shows a significant difference among racks or sets of flasks. Rack No. 1 on the average gives results which are 0.2 per cent (hide substance) lower than the results from the other racks.

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DETERMINATION OF HIDE SUBSTANCE IN LEATHER (provisional)

Nitrogen—Kjeldahl Method.

Reagents.

Concentrated Sulfuric Acid—Reagent grade conc. H_2SO_4, free from nitrogen, specific gravity 1.84, shall be used.

Sodium Hydroxide Solution.—Use a solution of approximately 11 *N* (for example: 450 g. sodium hydroxide pellets (98 per cent), or 600 g. sodium hydroxide flakes (76 per cent), dissolved in 1 liter of distilled water). Decant the clear solution from any sodium carbonate sludge which may separate out.

Copper Sulfate.—Reagent grade $CuSO_4 \cdot 5\ H_2O$.

Yellow Mercuric Oxide.—Reagent grade, yellow, HgO.

Boric Acid Solution.—4 per cent solution of reagent grade Boric Acid, free from borates. To each liter of solution, add 6 ml. of 0.1 per cent solution of Methyl Red and 4 ml. of 0.1 per cent Methylene Blue, both made up in 95 per cent Ethanol.

Sodium Sulfate,—Special Reagent grade, "free from Nitrogen", anhydrous Na_2SO_4.

Sodium Thiosulfate Solution.—8 per cent solution of reagent grade $Na_2S_2O_3 \cdot 5\ H_2O$.

Standard Acid Solution.—0.3 *N* acid (HCl or H_2SO_4) is recommended for Methods I & II; 0.12 *N* acid is recommended for Method III.

Preparation of Sample.

For Digestion Methods I and II (1.4 g. sample) the leather shall be ground in a Wiley Mill to pass a 4 mm. screen.

For Digestion Method III (0.5 g. sample) the leather shall be mixed thoroughly after the first grinding, and reground to pass a 4 mm. screen.

Digestion.

Method I. Place 1.4 g. of sample in a 650 ml. or 800 ml. Kjeldahl flask, add 10 g. of Na_2SO_4, 1 g. $CuSO_4 \cdot 5\ H_2O$ and 25 ml. conc. H_2SO_4. Place the flask in an inclined position, digest at moderate heat for about 10 minutes (to minimize sputtering), then at gentle boil until clear. Continue digestion for a further 2 hours. Cool, dilute with 250 - 300 ml. dist. water. Proceed to "DISTILLATION".

Method II. Place 1.4 g. of sample in a digestion flask and add 10 g. of a thorough mixture prepared by grinding together 7 g. of yellow HgO and 100 g. of Na_2SO_4. Then add 25 ml. conc. H_2SO_4. Digest at boil for 1½ hours total time. Cool, dilute with 250 - 300 ml. dist. water. Add 25 ml. of 8 per cent thiosulfate solution. Shake well and let stand at least 10 min. with occasional shaking. Then proceed to "DISTILLATION".

Method III. Place 0.5 g. of reground sample in a digestion flask, add 8 g. of the HgO-Na_2SO_4 mixture specified in II, and 20 ml. conc. H_2SO_4. Digest at boil for 1 hour total time. Cool, dilute with 250 - 300 ml. dist. water. Add 25 ml. of 8 per cent thiosulfate solution. Shake well and let stand at least 10 min. with occasional shaking. Then proceed to "DISTILLATION".

NOTE (1). At no time allow the flame to touch the sides of the flask above the level of the digest.

NOTE (2). If sputtering or foaming become excessive, the heat may be reduced but digestion time should be increased corespondingly.

Distillation.

Apparatus. The distillation apparatus consists of a bulb-trap connected to a vertical, water-cooled, condenser (of block tin, pyrex glass, or other material which has been shown not to react with hot dilute ammonia solution), to the lower end of which an extension tube is attached. This tube dips into the absorbing agent in a suitable container (beaker or Erlenmeyer flask). The connection between the trap and the con-

denser shall be so inclined that pools of condensate do not collect therein. All rubber stoppers and connections shall be well seated and gas-tight. The bulb-trap shall be properly baffled to prevent any alkaline spray from being carried over with the liberated ammonia. The Willits-John trap (J.A.O.A.C., **31**, No. 2, May 15, 1948, pp. 432-38.) and the cylindrical type with curved inlet and outlet have given good results.

Procedure. Measure, with a graduated cylinder, 125 ml. of 4 per cent boric acid solution (Digestion Methods I and II), or 50 ml. (Digestion Method III), and place it in the receiver, making sure that the outlet of the extension tube from the condenser is immersed. To the diluted solution in the digestion flask, add a few boiling chips (or other efficient boiling aid) and sufficient 11 *N* sodium hydroxide solution to make strongly alkaline. The volume required may be determined by adding a piece of litmus paper to the digest of a blank and measuring the volume of alkali required to change the color from red to blue. Use about 10 ml. in excess of this volume (too great an excess causes excessive bumping). For Methods I and II, 95 ml. is generally adequate, while, for Method III, 80 ml. is usually sufficient.

Pour the sodium hydroxide solution down the side of the flask so that it does not mix. Immediately connect the flask to the trap, taking care that the stopper is tightly seated. Mix the contents of the flask by swirling, and distil the liberated ammonia into the absorbing agent. Continue distillation until all the ammonia has been driven over; 150 - 200 ml. of distillate is generally sufficient. Disconnect the flask, wash down the condenser and delivery tube and dilute the distillate, if necessary, to approximately 350 ml. for Methods I and II or to 250 ml. for Method III. Titrate with the appropriate standard acid recommended under "REAGENTS" to first permanent pink. For the indicator recommended, the color change is green to gray to pink (pH about 4.90). A blank determination shall be run by the same method and using the same reagents, by substituting C. P. sucrose (free from nitrogen) for the sample of leather. If the distillate of the blank be green or gray, the volume of standard acid required to reach the end-point shall be deducted from the volume required by the sample. If the distillate of the blank be pink, sufficient standard alkali shall be added to turn the color green, and then the whole shall be titrated with standard acid as described above.

In this case, the difference:-

$$\frac{\text{ml. of standard alkali} \times \text{normality of alkali}}{\text{normality of standard acid}} - \text{ml. of standard acid}$$

shall be added to the volume of standard acid required for the sample.

$$\%\ N = \frac{\text{ml. of standard acid (for blank)} \times \text{normality} \times 0.14 \times 100}{\text{weight of sample}}$$

(corrected)

NOTE: Instead of distilling the ammonia into boric acid, and titrating with standard acid, it is permissible to distil into an accurately measured volume of standard sulfuric or hydrochloric acid and back-titrate the excess acid with standard sodium hydroxide solution, using the mixed indicator.

Hide Substance

The percentage of Nitrogen found, multiplied by 5.62, shall be taken as the percentage of Hide Substance in the leather.
Report results to 0.1 per cent Hide Substance.

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Fatliquor Distribution in Chrome - Vegetable Retanned Side Leather*

BERNARD ROLL

Moench Tanning Company

INTRODUCTION

A great deal of emphasis is placed on the distribution of oil through the thickness of leather as one of the requisites for a satisfactory fatliquoring operation. The factors controlling the distribution of oil in chrome tanned leather fatliquoring with sulfated oils has been the subject of many extensive investigations.[1, 2, 3, 4, 5] Consequently the conditions responsible for the degree of penetration of sulfated oils into chrome tanned leather are well established.

The relationship between physical properties of finished leather and oil distribution has also been the subject of much study, but here again the work was confined almost exclusively to straight chrome tannages.[6, 7, 8]

The previous history of a piece of leather prior to fatliquoring can have an important bearing on the takeup and penetration of a given fatliquoring.[9] Sulfated oils penetrate vegetable tanned leather more readily than they do chrome tanned leather[10]. There is some indication that a combination chrome - vegetable tannage resembles straight vegetable tannages in this respect.[11]

The present study is concerned with obtaining quantitative information on fatliquoring distribution in chrome - vegetable retanned side leather. Both anionic (sulfated oil) and cationic type emulsifying agents were investigated with a view toward elucidating the mechanism involved in fatliquor distribution for this type of leather. Fatliquor redistribution as a result of drying was also studied.

*Presented at the Forty Seventh Annual Meeting, The Griswold, Groton, Conn., June 13, 1951.

Experimental Procedure

Three groups of experiments were run on a pilot plant scale. Each group contained two experimental lots of leather—one fatliquored with a sulfated—raw oil mixture; the other with an emulsion composed of raw oil and a cationic emulsifier. Each experimental lot contained 100 lbs. (blue shaved wt.) of chrome - vegetable retanned side leather. The extent of the vegetable retannage is best described by the finished leather analysis which shows approximately 55 per cent vegetable retannage on the hide substance basis.

The fatliquoring of each lot of leather was carried out at 130° F., with a drumming time of 35 minutes and the fatliquor preparations diluted to 12 gallons. The following is a resume of the three groups of experiments with the percentage of materials based on the blue shaved wt. of the stock:

Group I

Experimental Lot IA	*Experimental Lot IB*
¾% Cationic Agent	2⅓% Sulfated Neats
3½% Raw Neatsfoot Oil	2½% Raw Neatsfoot Oil

The experiments in Group I were used as a starting point in this study because each of these fatliquoring formulae were known from experience to produce a satisfactory leather.

Group II

Experimental Lot IIA	*Experimental Lot IIB*
1½% Cationic Agent	3⅓% Sulfated Neats
2¾% Raw Neats	1¾% Raw Neats

In Group II we have increased the quantity of emulsifier 100 per cent over the quantity used in Group I, but the raw oil fraction is decreased in such a manner that the resultant fatliquoring contain the same total oil as in Group I.

Group III

Experimental Lot IIIA	*Experimental Lot IIIB*
4¼% Cationic Agent	5⅔% Sulfated Neats

The experiments in Group III were designed simply to substantiate the difference in distribution observed in Groups I and II.

The sulfated neats used in these experiments was a commercial variety containing 25 per cent moisture and 3.35 per cent combined SO_3. The cationic agent was cetyl dimethyl benzylammonium chloride. Considering the cationic agent a 100 per cent oil, it is apparent for all practical purposes that the total quantity of oil used in each experiment was 4.25 per cent.

With the exception of Experimental Lot IIIA, the principal variable in the above fatliquor preparations is the proportion of emulsifying agent to Raw Neatsfoot Oil. Hence any differences in layerwise distribution of the

oils in the various experiments may be ascribed to the quantity and type of emulsifying agent employed. Variance in pH will be considered later.

After fatliquoring, the sides were horsed up, allowed to drain for 1 hr., set-out, and sampled immediately after the setting out. It was felt that if setting out influences oil distribution in any way, the above procedure would better lend itself to practical intrepetation than by sampling before setting out.

The leather was paste - dried, washed, sammied overnight and then redried in a tunnel drier. At this point the sides were again sampled to determine the oil distribution in the dry leather. It has been shown in the case of chrome leathers fatliquored with sulfated oil that considerable redistribution of oil may take place when the leather is dried.

Oil content and distribution may vary widely over different areas of a single side. Therefore we sampled the butt and belly areas where these variations are greatest. All samples were split into six layers of equal thickness immediately after cutting them from their sides.

The layerwise samples taken in this manner were analyzed for oil and hide substance. Chloroform was the extraction solvent. In view of the fact that the Cationic Agent is a nitrogen containing compound it was necessary to run nitrogen determinations on all samples from Experimental Lots IA, IIA, and IIIA both before and after the chloroform extraction. The difference in the quantity of nitrogen, before and after chlorofom extraction, was significant only in those samples containing relatively great quantities of oil. In terms of hide substance these differences never exceeded 0.76 per cent.

Results and Discussion

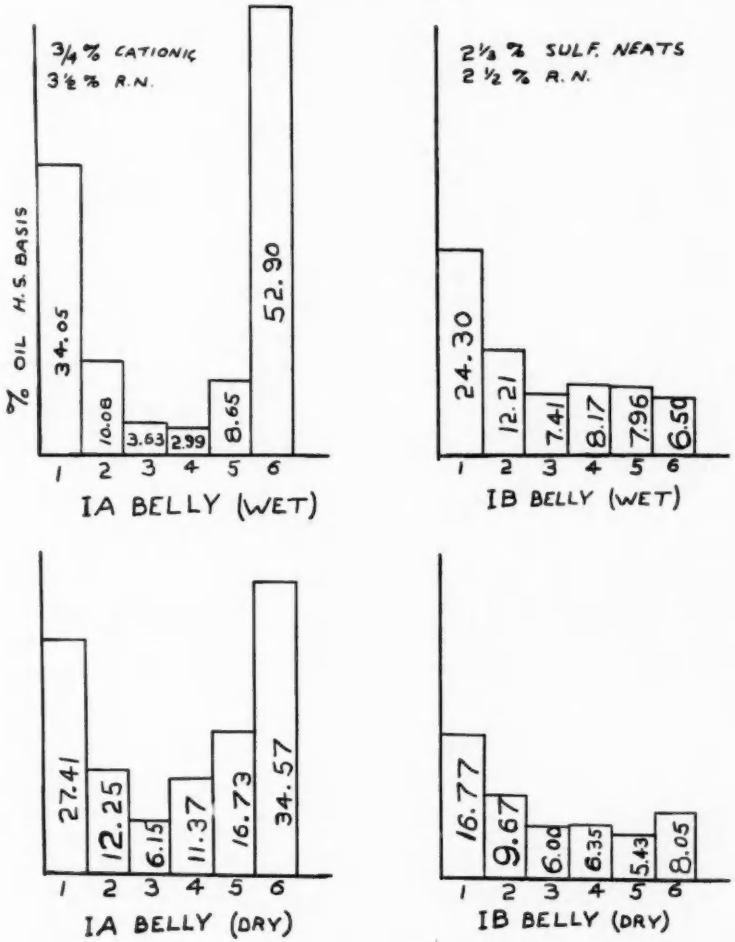
Figure I shows the oil distribution in the belly area of Experimental Lots IA and IB both in the wet and dry states. Percent of oil on Hide Substance Basis is plotted as a function of the respective layers, where Layer I represents the grain, Layer 6 the flesh etc.

The oil distribution for IA, both in the wet and dry leather, is very similar to distribution curves obtained when chrome tanned leather is fatliquored with sulfated oil type emulsions. The drying process resulted in a migration of oil from the outer layers toward the middle layers for the dried leather has considerably more oil in layers 3 and 4 than did the wet leather. The general shape of the distribution curve remains essentially the same, however.

The oil distribution for IB offers an interesting contrast, the most outstanding features being a relatively poor takeup of oil in the flesh layer and a heavy takeup in the middle layers. The distribution was not altered appreciably during the drying process.

Figure 2 showing the oil distribution for the butt area of IA and IB offers the same sontrast as observed for the belly area. Here IB has some semblance of a normal distribution in the wet state but does not compare very favorably with IA.

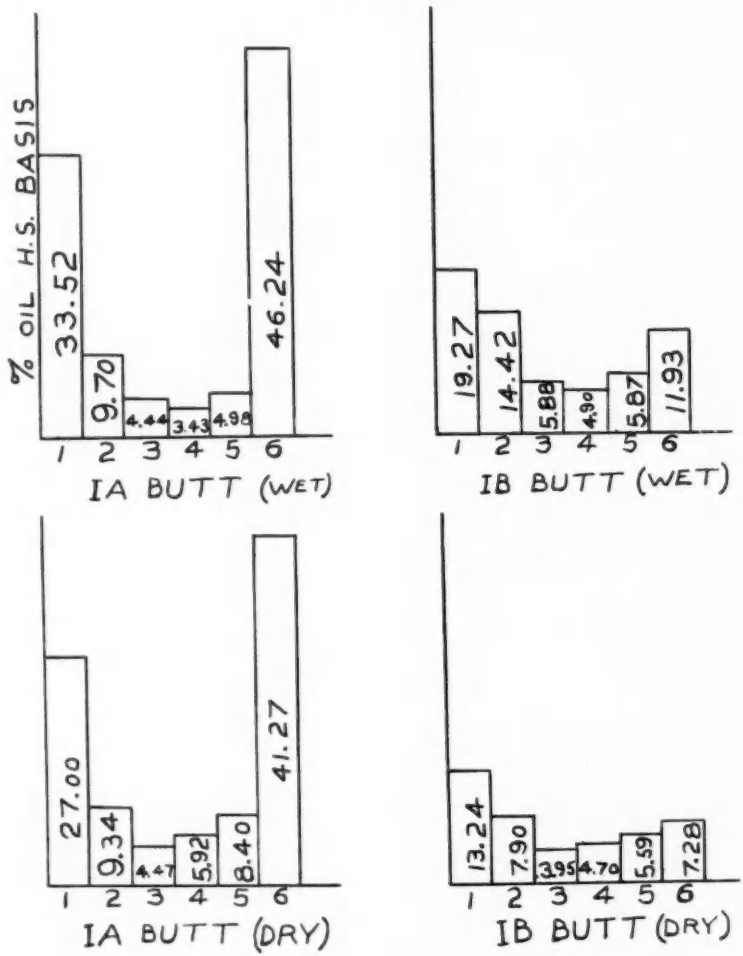
FIG. 1



The mean per cent of oil for the butt area of IA (wet) is 17 per cent while only 10⅓ per cent for IB. A similar discrepancy existed in the belly area. In view of this relatively poor takeup of fatliquor by Lot IB, it did not seem feasible to investigate the alternative of useing less sulfated oil.

The pH value of the spent liquor from Lot IA was 3.15 and IB had a pH of 4.20.

FIG. 2



EVALUATION OF THE FINISHED LEATHER FROM EXPERIMENTAL LOTS IA AND IB:

The temper of IA was firm and this leather had an exceptionally tight break throughout. IA was superior to IB from the standpoint of smoothness,

i. e., the drawn grain which usually accompanies this type of leather appeared to have been set-out better.

IB was slightly softer and mellower than IA, although the leather was generally satisfactory. There was a tendency for loose grain however, especially in the bellies and flanks.

FIG. 3

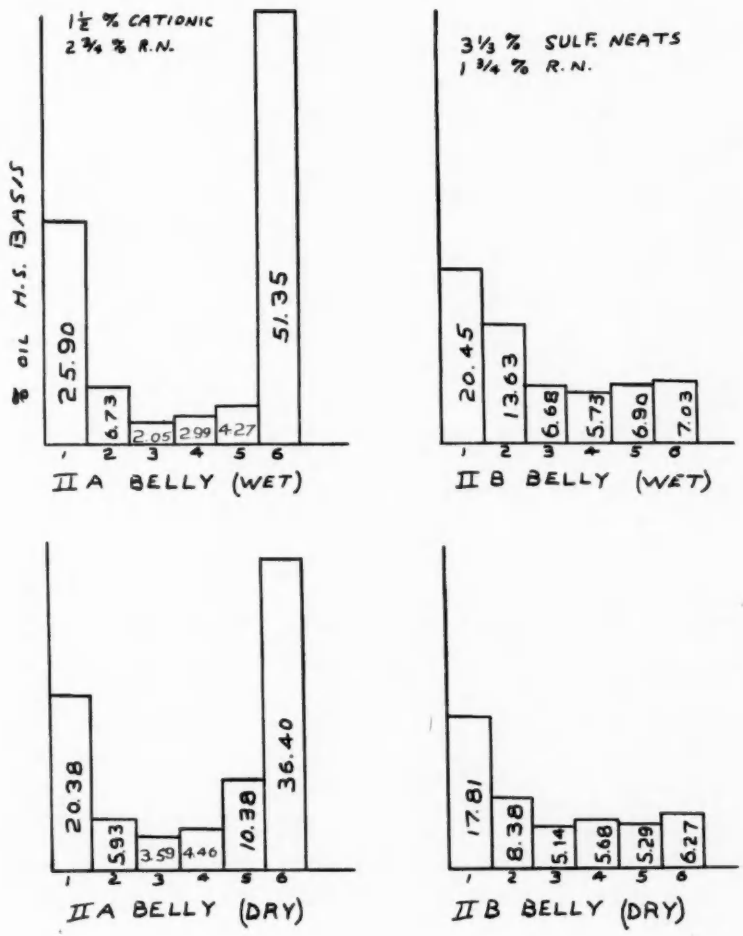
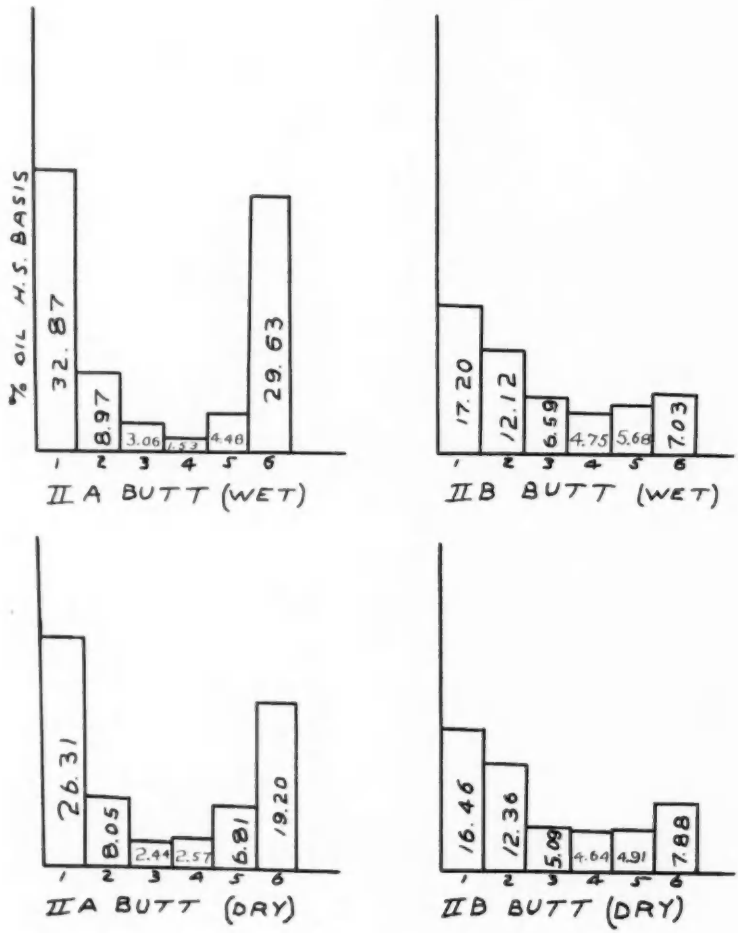


Figure 3 is a plot of the layerwise distribution of oil in the belly area of Lots IIA and IIB. Generally speaking the shape of these curves is similar to those of Figues 1 and 2, but it we compare the belly area of IIA with IA we see the establishment of an important trend. Increasing the quantity of cationic emulsifier 100 per cent has resulted in decreasing the penetration of

FIG. 4



the fatliquor. It has also resulted in lessening the migration of oil toward the middle layers during the drying process.

Comparing IIB with IB demonstrates that a 100 per cent increase in the quantity of sulfated oil results in no significant change in oil distribution through the thickness of the leather.

Figure 4 showing the oil distribution for the butt area of Lots IIA and IIB merely reflects the observations made for the belly area of these same lots.

The spent liquor from IIA had a pH of 3.20 while IIB had a pH of 3.75.

Evaluation of the Finished Leather From Experimental Lots IIA and IIB:

IIA was very much firmer than IIB; it was also firmer than IA. The break was very tight - comparable to IA in this respect. From the standpoint of smoothness IIA was decidedly superior to IIB.

IIB was comparable to IB with regard to temper, but there seemed to be an increased tendency toward loose grain.

Figure 5 shows the oil distribution for the belly area of Experimental Lots IIIA and IIIB. IIIA substantiates the trend observed in IA and IIA, namely the cationic emulsifier is taken up by the outer layers when applied to the type of leather under consideration. The distribution for IIIA probably represents the ultimate if it is desired to keep the middle layers of the leather free of oil. Note that there was practically no migration of oil toward the center during the drying process.

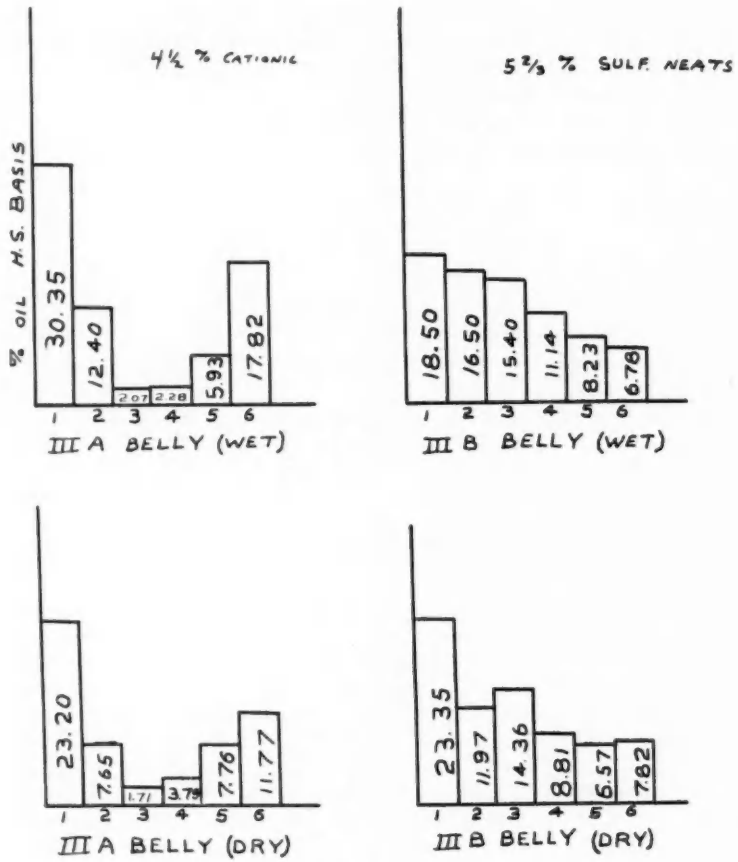
The remarkable distribution of oil in the wet leather of IIIB offers a clue to the mode in which sulfated oil penetrates this type of leather. It appears that the oil penetrated through from the flesh side very readily, but was retarded as it reached the denser thermostat and grain layers. The distribution obtained in the belly area of IB and IIB hinted at the same mechanism, but it is much more pronounced in the present case, IIIB.

It should be noted that in going from IA to IIIA in the cationic series, an increase in the amount of cationic emulsifying agent results in progressively less oil being taken up by the leather. In the anionic series however, there was no significant difference in fatliquor takeup in going from Lot IB to IIIB.

The pH value of the spent liquor from IIIA was 6.2 while IIIB had a pH value of 5.5, thus dissipating the possibility of differences in pH being responsible for the contrasting oil distributions obtained from the cationic and anionic emulsions.

Figure 6 is a plot of the oil distributions obtained for the butt area of IIIA and IIIB and here again the butt area is simply a counterpart of the belly area.

FIG. 5

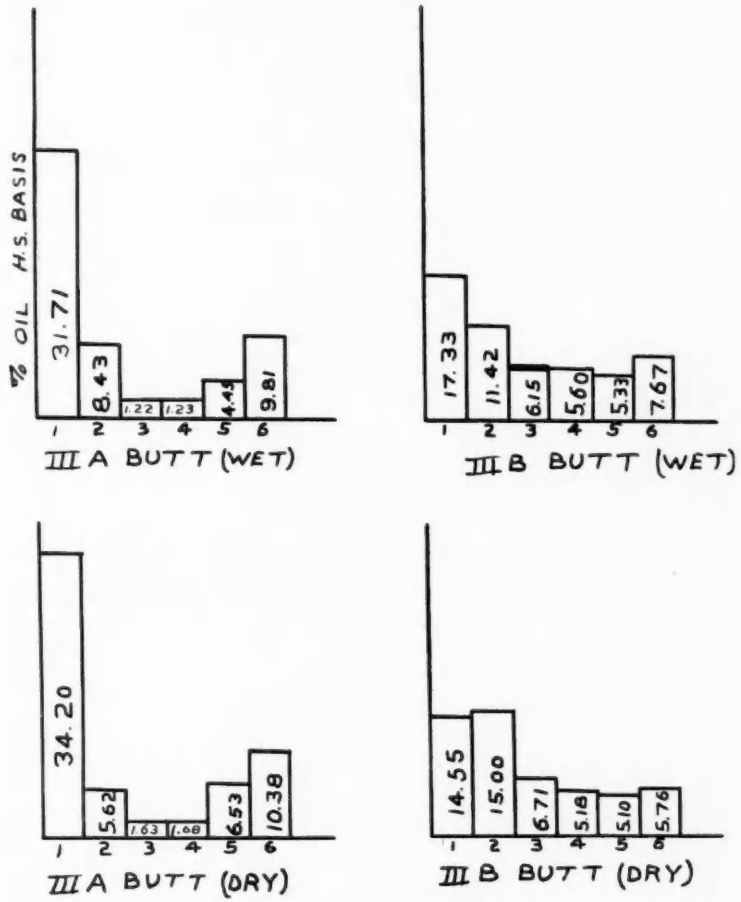


Evaluation of the Finished Leather From Group III:

IIIB was extremely soft and loose breaking. The temper resembled garment leather more than shoe upper. There was considerable drawn grain contrasting sharply with IIIA which was smooth.

IIIA was not a satisfactory leather, however. It had an extremely hard—almost unnatural feel. Surprisingly enough, in view of the fatliquor distri-

FIG. 6

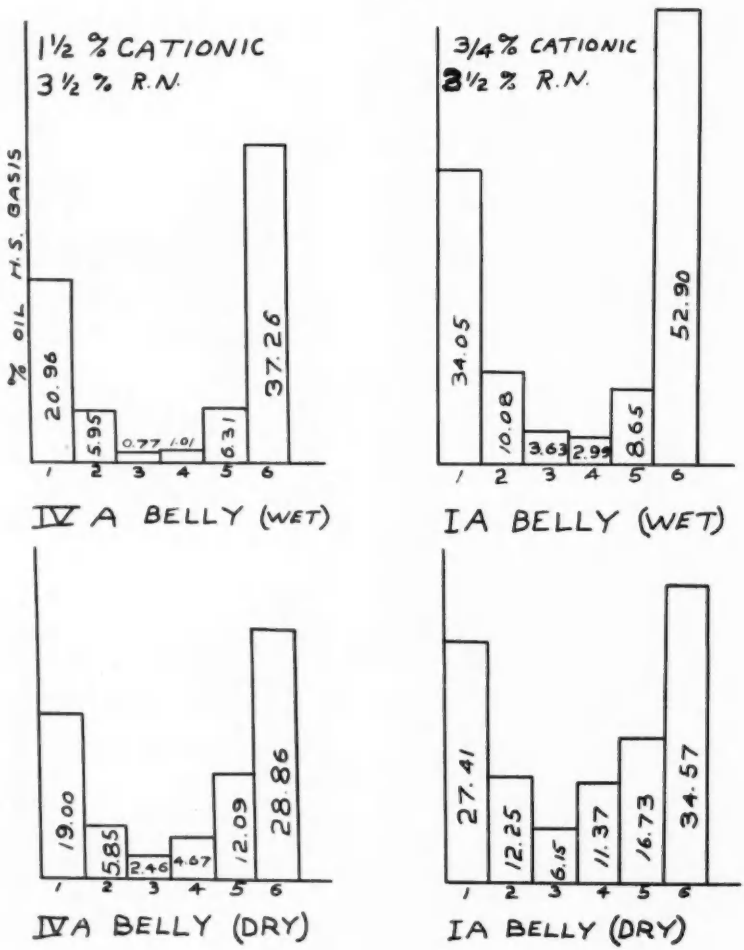


bution, the grain was extremely loose and pipey. The leather from IIIA gave the impression of not having been lubricated. Recalling that IIIA received no lubricating material other than what might be derived from cetyl alcohol, the result is not too surprising [1].

At this point it was apparent that two factors were operating independently and simultaneously in the A series of experiments.

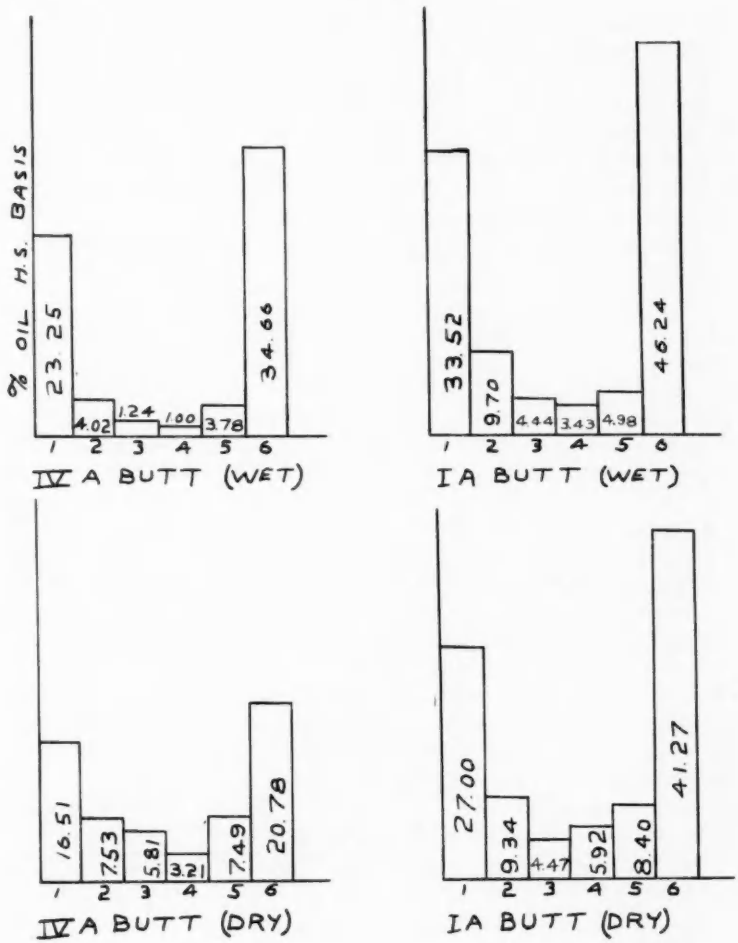
1. The quantity of effective lubricating agent (Raw Neatsfoot) was diminished in going from IA to IIIA.
2. The tendency for less fatliquor to reach the middle layers of the leather increased in going from IA to IIIA.

FIG. 7



The finished leather, with respect to firmness, rated in the order IIIA > IIA > IA. Therefore it was necessary to attempt to learn which of the above factors was most responsible for the fact that increased quantities of cationic emulsifier made for firmer leather.

FIG. 8



The A series was extended by running a fourth Experimental Lot, IVA, in which the fatliquor was composed of 3.5 per cent Raw Neatsfoot Oil and 1.5 per cent Cationic emulsifier. This is the same quantity of Neatsfoot used in IA, but twice as much emulsifying agent. Fig. 7 shows the fatliquor distribution in the belly area of IVA, and the distribution for the same area of IA is also given for ease of comparison.

The mean per cent of oil in IVA (wet) is 12 while IA has 18.5 per cent. The tendency for less oil to be taken up in the middle layers by increasing the ratio of emulsifying agent to raw oil is again apparent.

Fig. 8 is self explanatory.

Now the finished leather from IVA was definitely firmer than that of IA. Hence by using a given quantity of Neatsfoot oil with the cationic emulsifier we can expect relatively firmer leather by increasing the ratio of emulsifier to Raw Neatsfoot. Two reasons can be advanced for this phenomenon:

1. The oil distribution tendency observed above.

2. Relatively great quantities of cationic emulsifier diminish the takeup of fatliquor.

Summary and Conclusions

The behavior of cationic emulsions on the type of leather under consideration may be summarized as follows:

1. The fatliquor is taken up predominately in the outer layers while the middle layers receive relatively little. This effect is accentuated as the proportion of emulsifying agent to raw oil is increased.

2. There is some migration of oil toward the middle layers when the leather is dried, but the extent of this migration is diminished by increasing the proportion of emulsifying agent to raw oil.

3. Takeup is greater in the flesh layer than in the grain layer except when relatively large quantities of emulsifier are used.

4. Increasing the ratio of emulsifying agent to raw oil does not make for greater softness in the finished leather. This is probably a consequence of item 1 above as well as item 5 below.*

5. When the ratio of emulsifying agent to raw oil was .75 to 3.5 the takeup of fatliquor was practically complete. Increasing this ratio resulted in progressively less fatliquor being taken up.

6. A greater quantity of oil is extractable from the wet leather than from the same leather after drying. There does not seem to be a direct relationship between this quantity of oil which becomes "fixed" and the composition of the fatliquoring emulsion.

*This observation does not coincide with an earlier view dealing with the use of cationic emulsifying agents in fatliquoring.[12]

It is therefore evident that the behavior of a cationic fatliquor on chrome - vegetable retanned leather resembles the behavior of sulfated oils on straight chrome tannages.

Sulfated oil emulsions react so differently with chrome - vegetable retanned leather compared to their reaction with straight chrome tannages, that there is no basis for comparison. With respect to chrome - vegetable retanned leather however, the following generalizations may be drawn:

1. Sulfated oils, either alone or in combination with raw oil, tend to penetrate into the interior of the leather. It is not unusual for the middle layers to contain as much oil as the flesh layer.

2. Within very wide limits the proportion of sulfated oil to raw oil may be increased without substantially affecting either the takeup of fatliquor or its distribution within the leather.

3. Migration of oil during the drying process does not alter appreciably the comparative oil distribution obtained in the wet leather.

The tremendous difference in fatliquor distribution obtained in the foregoing experiments can be best explained on the basis of the cationic emulsifier having a greater affinity for vegetable tanning materials than sulfated oils do. Sulfated oils are known to combine with straight chrome tannages. Perhaps the fact that the active constituent of a sulfated oil is an anion, while chrome tannage carries a positive charge, is of fundamental importance. We could then apply the same reasoning in hypothesizing a reaction between a cationic emulsifying agent and vegetable tanning material for in this case the emulsifying agent is positively charged while the tannage is anionic.[13,14]

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Discussion

B. A. Grota: I wish to thank Mr. Roll for his presentation of a paper that includes some previously unpublished data of considerable interest.

We will discuss this new cationic emulsifier first. The study of the fatliquoring of different types of leather is unique. The type used in this work is not chrome leather and not exactly vegetable and has a few of the characteristics of each, but is still a separate entity in itself, and for the most part cannot be treated as being chrome or vegetable, but has to be treated as something separate. Perhaps the cationic emulsifiers are well suited for fatliquoring this unique leather.

I have one question I would like to ask Mr. Roll: You demonstrated that oil migration during drying decreased with increased quantities of emulsifier.

Do you believe that it is mostly the raw oil which moves during drying, that the emulsifier stays more or less in one region?

B. Roll: I believe that is correct because you will recall that we ran Kjeldahls on the leather before and after extracting the oil. In this way we hoped to determine nitrogen derived from collagen as well as nitrogen derived from the emulsifying agent. The latter quantity did not vary appreciably for any of the layers before and after drying the leather.

Mr. Salamatov: When you plot your distribution on dry leather, I would like to know whether or not the dry leather had been flexed, staked or just dried?

Roll: No flexing, no staking. The only mechanical handling would have been the pasting operation. It might introduce a slight amount of flexing but nothing that you could avoid in practice.

K. Klanfer: What is the difference between sulfonated emulsion and raw oils experiments regarding the cationic emulsions from soap and raw oil?

Roll: If I understand your question correctly, you wonder how soap - raw oil fatliquors compare with the cationic - raw oil type on the kind of leather under consideration. Our experience with soap - raw oil fatliquors indicates that their behavior parallels that of sulfated oils. If a sufficient quantity of soap is used to give an emulsion of fine particle size the fatliquor tends to penetrate freely. If an emulsion of relatively coarse particle size is used, that is employing a minimum quantity of soap, the fatliquor penetration can be retarded. Under these conditions the fatliquor can be taken up competely, but it takes up preferentially in the flesh rather than in the grain. Thus, although the leather may contain a normal amount of oil, the grain may not be well lubricated. You may then have the problem of cracky grain which is always a hazard in this kind of leather.

R. QUARCK: I have a question. In comparing a sulphated oil with a cationic emulsifying agent, you use a specific sulphated oil, but I think most act rather similarly.

In using one specific cationic agent, do you think what you have been demonstrating is the principle of the cationic agents as such, or of one specific compound? In other words, have you tried other cationic compounds and found a similar trend?

ROLL: We have worked with many cationic emulsifiers and find that they differ in degree rather than in kind. I think in this application we have to consider two points when choosing a cationic emulsifying agent:

1. It should be an efficient emulsifying agent.
2. Its degree of cationic activity.

Not all of the fatty amines are strongly cationic. Some work more like non-ionic emulsifiers—which are something else again.

A. J. MAY: Were any tests made in getting the burst strength or tearing strength of various leathers?

ROLL: We ran bursting strength tests but not tensile strength or stitch tear. The bursting strength was significantly weaker for experimental lot 3A. Lot 3B was strongest. Lot IA compared favorably with IB and IIA compared favorably with IIB.

C. E. RETZSCH: I would like to ask Mr. Roll if he has worked with sulfated oils of differing degrees of sulfation, or if he has done any work using combinations of sulfated oil and cationic emulsifiers. What I am thinking about is a low sulfated oil plus a cationic agent—whether something like that has been investigated?

ROLL: We didn't work with oils at various degrees of sulfation. Neither have we done anything with fatliquors containing both a sulfated oil and a cationic agent since the two usually precipitate. But we have observed some interesting effects by treating the leather with a small amount of sulfated oil followed by a cationic - raw oil fatliquor. The sulfated oil takes up preferentially in the grain, which seems to be a general occurence for any fatliquor of fine particle size. Now if the cationic - raw oil combination is added to this leather, it also takes up preferentially in the grain, which is quite different from the distribution obtained in Lots IA and IIA. The net result of using a sulfated oil ahead of the cationic fatliquor is to get more oil in the grain.

Of course all of this is in line with our hypothesis that the deposition of the cationic fatliquor in the outer layers of the leather is a result of those layers containing a preponderance of anionic materials.

S. S. KREMEN: Are these differences due just to fundamental differences in kinds of emulsifiers, or do the two types of emulsifiers give a vastly different range of particle sizes?

ROLL: I think that both emulsion particle size as well as the charge carried by the emulsifying agent are important in determining fatliquor distribution. Of course the materials with which the leather has been treated prior to fatliquoring have an important bearing.

Particle size is important, but in lot IIIA where we used the cationic agent without any additional oil we were working with particles approaching the dimensions of a true solution; yet in that case we had less fatliquor penetration than in any of the other experiments using a cationic fatliquor.

Lot IIIA was also the only experiment in the cationic series in which there was a greater takeup of oil in the grain than in the flesh indicating again that particle size is important in determining whether a given fatliquor shall take up preferentially in the grain or in the flesh.

W. LOTZ: In preparing the stock for this fatliquor, we can assume you are using a straight vegetable retan; that is, you are not using either synthetic or the so-called replacement materials or tans which then affect the fat distribution in the grain leather. Do you use straight vegetable tanning or do you use a combination?

ROLL: If you are thinking of the influence of the $SO_3^=$ groups on fatliquor takeup and penetration, there were two materials used in the retannage which might have been important, bisulfited quebracho, and a so-called spruce extract.

Retaining chrome leather with any anionic agent, whether it be a syntan, replacement tan, or vegetable extract, tends to make a cationic fatliquor takeup in the outer layers of the leather. It's the principle of the leather assuming a negative charge while the emulsifier portion of the fatliquor is positively charged.

BOOK NOTICE

The Leather Manufacturing and Related Industries in Germany During the Period 1934-1945. (British Intelligence Objectives Sub-Committee Surveys Report No. 27). By C. H. Spiers, with Foreword by J. R. Blockey. His Majesty's Stationery Office, London. 138 pages. 1950. Price 3s. 6d.

Following the military collapse of Germany in 1945, the American, British, Canadian and Indian governments dispatched intelligence teams to study the German leather industry, particularly the wartime developments thereof. The results of these studies were published in a series of reports,—for example, the well-known Schultz-Schubert report—which overlap considerably. Dr. Spiers has done the leather industry a valuable service by condensing and consolidating the mass of information that these reports contain, and presenting the result in a compact and usable form. A tanner who wishes to learn what methods of unhairing were used in Germany will no longer have to obtain and peruse a half dozen reports; he will find a digest of all the information on unhairing, from all the reports, condensed to 2 or 3 pages.

Following the foreword by Prof. Blockey, and a brief introduction, the next 110 pages are devoted to some 87 topics, arranged alphabetically. Liberal cross-references are provided; thus Blancorols A and B are mentioned under Aluminum Tanning, Chemicals, Fur Tanning,

and White Leathers. While the treatment of each topic is necessarily brief, a surprising amount of information is packed into a few lines, and full references are given to the original reports. A 6 page bibliography of all the intelligence reports and an 8 page index add to the value of the work. There is also a list of the tanneries visited, and by whom.

Many items have been taken from reports that do not pertain specifically to the leather industry,—for instance, those on dyes and other synthetic chemicals.

To quote Prof. Blockey's foreword: "It is difficult to assess what the value of these reports may be to the industry in general or to the individual firms in particular. It is always difficult to translate or apply technical operations from one tannery to another, especially as complete processes, but most tanners will find—facts and descriptions—among the reports which will be of definitive value.

"The Reports, taken together, present a fairly complete picture of one country's leather industry and form a valuable compendium of modern manufacturing methods."

H. B. M.

ABSTRACTS

Some New Investigations in the Valonia Field. By O. Gerngross. *Oesterr. Leder-Zeitung*, **5,** 387 (1950). A review of recent work. Valonia gathered at the proper time has been found to have a tannin content of as high as 46 percent (49.4 percent by the filter method) and a non-tannin content of 11.4 percent. Valonia has a two-year ripening cycle. When an undamaged cup is separated into layers from outside (beard) to inside, a decrease of tannin of as much as 30.7 percent is found. As the inner parts are youngest, it appears, that the youngest vegetative layers are lowest in tannin. Eitner found that the tannin content of the whole valonia decreased with age. I. D. C.

The Reaction of Hexa-Urea Chromic Chloride with Collagen. By K. H. Gustavson. *Oesterr. Leder-Zeitung*, **5,** 383 (1950). Hexa-Urea chromic chloride has the coordination number of chromium, in the cationic chromium complex, entirely satisfied by six firmly attached molecules of urea. In water, the compound does not hydrolyze or form aggregates. It could not tan, provided the theory were correct, that in chrome tanning the chrome complexes attach to the hide protein by means of coordinate valencies on the hydroxo group of the complex. Stiasny concluded that it did not tan, but he treated hide powder only 4 hours with the chrome solution.

By prolonged treatment (2-4 weeks) of hide powder or pelt with a solution of the complex salt containing 6.7 grams of chromium per liter, an increase in shrinkage temperature (Ts) of 20° was observed. Irreversibly fixed chrome was of the order of 10 percent Cr_2O_3 on the collagen basis. The acidity at the end of the tanning period was approximately 100 percent [basicity 0 percent], indicating no hydrolysis had occurred. Addition of urea to make the tanning solution 4 molar in urea had almost no effect on fixation. Urea would repress hydrolysis, so tanning does not depend on hydrolysis of the complex salt.

To ascertain the behavior toward urea of leather tanned with hexa-urea chromic chloride, leather containing 2 percent Cr, in which the acidity of the chrome collagen compound was 96 percent, and with a Ts of 88°C was treated 14 days in 8 molar urea solution. The washed leather had a Ts of 83° and a Cr content of 1.4 percent. Regular chrome leather resists the action of urea, therefore at least a part of the hexa-urea compound fixed by collagen exists in a form different from that of simple sulfato-chromium complexes. When passed through a cation exchange resin, the complex chrome cation is very firmly held by the organolite and is only partly removed by repeated percolations of 5 molar hydrochloric acid. The hexa urea

compound holds a unique position among the chrome tanning agents. The possibility of a multifunctional coordination of the amido groups of urea in the chromium complex on the carbonyl oxygen of the peptide groups of adjacent chains is suggested. I. D. C.

On the Structures of Fibrous Proteins I. By Y. Kanda. *Bull. Chem. Soc. Japan*, **23**, 137 (1950). The author proposes a diagramatic explanation for the polypeptide structure of a α-keratin.

On the Structures of Fibrous Proteins II. By Y. Kanda. *Bull. Chem. Soc. Japan*, **23**, 143 (1950). The author has determined and shown diagramatically the polypeptide structure of feather keratin, β-keratin, silk fibroin of *Bombyx mori*, silk fibroin of *Saturnia pyri* and silk fibroin of *Antheraea mylitta*.

Common Causes of Leather Defects. By H. W. Thomas. *Shoe and Leather Reporter*, **262**, No. 11, 13 (1951). Most of the causes of common leather defects can be traced to changes in processing whereby the process chain is upset. Correct processing is considered to be the result of three factors, namely, temperature, time and chemicals. Loose grain is usually the result of too long soaking, or soaking at too high a temperature. Overliming or oversulfiding can also cause loose grain. Lime blasted hide can be overbated under the layer of calcium carbonate and later show loose grain as a result of the enzyme action. Loose, spongy leather can result from a too basic tannage early in the stages of the chrome tanning operation. A low pH pickle, followed by a normal chrome liquor, tends to give the results of basic tannage. Another cause of loose leather is the fixation of too much chrome in the grain. Fat liquor can also produce loose leather through improper distribution of the fat liquor in the layer-wise structure of the leather. A choice of fat liquors is important since some have a tendency to penetrate too deeply, causing an over-nourished and soft center layer, but a firm grain. Drawn grain in chrome leather, especially the "bellydraw", extending parallel to the backbone, is usually caused by improper soaking and liming. Soaking should be thorough. Pebbled grain is regarded as another form of drawn grain. In chrome leather the cause is usually attributed to insufficient salt in the pickle, or excessive milling. It is more common in vegetable leathers, and here excess milling is the cause. Tender grain is characterized by low elasticity, low tear resistance and little fibrous structure. The cause of tender grain is any process deficiency which tends to prevent proper opening up of the grain layer, tends to prevent the removal of non-leather making substances in the grain layer, or tends to plug or otherwise overload the grain layer which has been properly conditioned in earlier stages. In the case of chrome leathers, about 75 per cent of the causes of tender grain are found in the series of processes up to and including bating, 10 per cent have a partial origin there, but are contributed to by later operations, and the final 15 per cent are caused by deficiencies in the process from the pickling on. In the case of vegetable tanned or so-called combination tanned leather, experience has shown that about 50 per cent of these causes of tender grain originate in the processes up to and including bating, while the other 50 per cent occur in later operations. The author cites a case of tender grain in a certain chrome leather which on investigation was traced to too cold soaks and limes with consequent underprocessing in the beam house. In a vegetable leather with tender grain, it was found that drum temperatures were excessive, causing too rapid fixation of tannin.

Iron Tanned Sole Leather. By V. Schmitt. *Leather and Shoes*, **120**, No. 16, 12 (1950). The author describes the tannage and properties of sole leather pretanned with Ferrigan P and Ferrigan PN, followed by after tannage with syntans.

Production and Marketing of Colonial Hides and Skins. By J. R. Furlong. *Colonial Plant and Animal Products*, **1**, 271 (1950). The present article deals with the production, preparation and marketing of Colonial hides and skins. In most of the countries, the hides and skins for export become available in ones and twos at places spread out over very large areas. The quantity obtained from abattoirs in towns represents only a small percentage of the export. Itinerant native collectors travel long distances to collect the hides and skins, which are then sold to middle men in the small towns, who in turn dispose of them to the exporter at his up-country depot, or at the post. The scattered production of these materials makes it extremely difficult to effect improvement in preparation. In many parts of Africa the major portion of exported hides is from fallen animals. Nigeria is the most important producer among the Colonies, followed by Kenya, Tanganyika and Uganda. Somaliland ships Berbera Blackhead sheepskins, which go into glove leather. While the Folkland Nigeria is of very high standard, that at Lagos on the Coast is often very poor. The same variation is to be found in East Africa. It is attributable to unskilled employees and the practice of cleaning the hides of excess flesh, during which operation the stock is frequently cut and gouged. Because of the scarcity of salt in East and West Africa, hides and skins are given a straight air-drying. Abattoir hides are dried on frames in a shed, and are usually well cured. Natives cure their stock by staking, hair side down, in unshaded areas. In the dry season the hide becomes flint dry in three or four days, but in rainy weather as long as ten days may be required. Ground-drying may give rise to degradation of the hide substance, the damage being known in varying degrees, and termed blister, taint and hair slip. The first two represent relatively mild forms of damage and in a more pronounced form give rise to loose grain. Blister is descriptive of deterioration between the hide surfaces.

In 1930 The Imperial Institute Advisory Committee on Hides and Skins recommended a comprehensive study on the causes of blister and means of preventing it. These studies were begun in Kenya in 1932 in cooperation with the Veterinary Department. It was found that restricting the drying to one surface of the hide was conducive to blister and taint, and that by exposing both sides of the hide to free circulation of air, perfect drying without damage could be obtained. The results showed that the sun was not the cause of the damage. The trials further showed that drying on frames eliminated damage, but because of the scarcity of frame material in many localities, this practice could not be generally adopted. Trials are now in progress to find a method of suspension which will be generally applicable. One such suggestion is the use of long pegs which will suspend the hide above the ground, while another is suspension over a thin rope or wire, with the sides of the hide or skin held apart. The latter has found general application in Nigeria and East Africa in the case of goat skins with satisfactory results. Another cause of damage is failure to stretch hides to dry immediately after flaying.

The Northern Provinces of Nigeria grow cattle of the humped type. Kano is the great collecting center in the North for cattle which, after inspection, are dispatched by rail to the towns and cities of the South where they are slaughtered for food. In the larger centers the green hides are taken over immediately by the shippers, in whose depots they are arsenicated by immersion and dried by the suspension method. The Nigerian position is much more satisfactory than the East African. The large number of French hides brought across the border into Northern Nigeria are liable to be of inferior take-off and cure. In the early twenties Nigerian goat skins had a poor reputation, but through propaganda and instruction, the quality improved so that they are recognized as among the best on the world's market. The finest of these are the Sokoto Reds, followed by the Kano skins, and then the Bornu. The skins are dried by placing them over a line in a shed, which has a grass roof and wire mesh sides. Nigeria sheep are of the hairy type. Nigeria possesses a tanning industry which is worth noticing. It is situated in the Northern Provinces. It is carried on by natives on a small scale, the tanneries often being located in back yards. The quality of

leather produced is of a useful standard. Liming is accomplished with the ash of the Mariki tree. Puering is with pigeon dung. The tan liquor is made from crushed pods of Bagaruwa *(Acacia arabica)*, including the seeds. After tanning, the skins are washed, oiled with groundnut oil, and dried over a line. They are staked by drawing them between the foot and a flat stone. Softening is effected by beating several skins in a bundle against a smooth stone. This local tanning industry has big potentialities. A firm of exporters has recently erected a tannery which they themselves operate. It follows generally the local practice, but uses lime instead of wood ashes, and introduces paddles and tanks.

In East Africa the hides are usually of poorer take-off than in Nigeria, since most of the cattle are slaughtered by occasional individuals. The cattle are of the small humped type, known as the Zebu breed. A larger breed without humps is designated Aakole, and in addition there are some representing a cross between native stock and European cattle. Hides are ground-cured or by the suspension method. Shed drying is practiced to some extent, but it has not proved practical. East African hides are usually light, heavies weighing twelve pounds and over constituting but 25 per cent of the total production. These come mainly from Uganda. The reputation of East African hides and skins is related to the ports through which they are exported, those passing through Mombasa having a better reputation than those exported from Dar es Salaam. This gave rise to sending the best Tanganyikas through Mombasa to collect the premium attached to Mombasa products. Now certification of origin is compulsory, Uganda skins being branded with a "U" and Tanganyika skins with a "T". Before World War I East African hides were bought on the Continent, but in the Second World War British tanners were forced to take them. They were surprised at the improvement in the raw stock.

East African goat skins are used for the same purpose as the Nigerians, but at their best do not challenge the outstanding Red Sokoto skins from Nigeria. Kampalas have a good name, while ordinary Mombasas are less desirable. Tanganyika produces the Moshi-Arusha which are some of the best dried goat skins of East Africa. Sheepskins from East Africa are of the hair type, and are as a whole of poor quality. In Kenya and Uganda the exporters operate up-country, but in Tanganyika they are established on the coast only. Grading takes place at the collecting centers but final grading for export is made at the port. Arsenication by spray is practiced at the port. Sheep and goat skins constitute about 60 per cent of Somaliland Protectorate exports. Production of cattle and camel hides is of minor importance. Berbera Blackhead sheep skins are of little value for finishing on the grain side because of the scars and thistle scratches near the grain. Skins are removed from the carcass by the cased method and cured by sun drying. America receives the bulk of these skins to be made into suede leather. Northern Rhodesia has an export trade in cattle hides and the Falkland Islands in sheep skins. Malaya is the chief source of buffalo hides. Nigeria and Malaya supply reptile, crocodile and lizard skins.

Solubility of Commercial Para-Nitrophenol in Oils and Greases. By H. B. Merrill. *Shoe and Lea. Reporter*, **263**, No. 7, 22 (1951). At the request of the Committee on Leather Research of the National Research Council the author made a study of the solubility of para-nitrophenol in ten oils and greases. He found that the solubility of para-nitrophenol in neatsfoot, cod, corn and cottonseed oils, tallow and wool grease exceeded 20 per cent on the weight of the oil at 175°F., and is 10 per cent or slightly more at room temperature (about 70°F.) for the four oils. Tallow and wool grease apparently hold 20 per cent dissolved para-nitrophenol at room temperature. Para-nitrophenol is practically insoluble in mineral oil or paraffin. Para-nitrophenol is soluble in Vac-grease and Vac-grease W to an extent greater than 10 per cent at 175°F., but these materials are unsuitable for preparing a stock mixture. Easily oxidized oils—cod, Vac-grease D, and to a lesser extent, cottonseed oil, react with

para-nitrophenol on heating to form a small amount of a dark brown gummy material. None was formed with neatsfoot oil, tallow or wool grease.

New Leather Lamination Methods. By T. A. Dickinson. *Leather and Shoes*, **121**, No. 22, 10 (1951). There is a tendency today toward unsaturated thermosets or thermoplastic monomers and polymers in place of solvent dispersed resins in making leather laminations. The purpose of the new lamination procedure is to speed up production with less labor.

Evaporation Coating Leathers. By T. A. Dickinson. *Leather and Shoes*, **122**, No. 8, 8 (1951). Evaporation coating is a process whereby leathers can be rigidly or flexibly, transparently or opaquely, surfaced with metallic and non-metallic materials for a variety of functional and decorative purposes. It consists of heat vaporizing coating materials with high melting temperatures and surfacing leather with these. The vaporized coating particles are of molecular dimensions and subject to rapid chilling after contacting a leather deposition surface. Coatings of a millionth of an inch are possible. Vaporization of the coating material and the deposition surface are enclosed in a vacuum, which can be subsequently filled with an inert gas to prevent oxidation of the deposited metallic film. Such films are credited with increasing scratch resistance of the leather from 25 to 150 per cent. Aluminum coated fabric has been used successively in Arctic clothing of light weight. The thickness of an evaporation coating depends on the time a deposition surface is exposed to vaporized coating materials.

Britain's Shoe Research Program. By H. Bradley. *Lea. and Shoes*, **122**, No. 9, 10 (1951). The British Boot, Shoe and Allied Trades Research Association was started at Northampton in 1919 with a part-time staff and a trade contribution of $2,000 a year. In 1922 a full-time director was appointed, headquarters were moved to London and a beginning made with full-time work in incommodious premises. In 1927 a move was made to better quarters. These were damaged in the air raids of 1940, and the Association went to temporary quarters in the Boot and Shoe School at Kettering. At the close of the war search was made for a suitable location in the Midland area, and in 1947 a property was purchased in Kettering, the new laboratories being known as Satra House. Today, the whole shoe industry of Great Britain is connected with the Research Association. Manufacturers, wholesale and retail distributors, Shoe Operatives Union, and many supply houses have full or affiliated memberships. The research program starts with foot surveys to accumulate statistical knowledge of foot dimensions and shapes for all sections of the community and age of the subjects. Orthopedic aspects of foot wear and physiological questions relating to foot comfort in regard to warmth, coolness, moisture dispersal and the like come in for investigation. Properties of materials entering into shoe manufacture are examined. Methods of shoe manufacture are studied. In fact, the Association is pursuing a course of study which comprehends all phases of shoe manufacture, materials of construction and the reaction of the wearer to the finished product.

New Leather Inspection Methods. By T. A. Dickinson. *Lea. and Shoes*, **122**, No. 11, 14 (1951). The author proposes the use of radioisotopes, ultrasonic reflectoscopes, special coatings and refrigeration equipment as new and useful devices for testing leather. Several specific pieces of equipment are listed.

Testing Leather for Footwear. By W. T. Roddy. *Leather and Shoes*, **122**, No. 13, 11 (1951). By applying certain physical tests to leather, such as stitch tear, tongue tear test, tensile strength, and resistance to grain crack, the fitness of the leather for its specific use can be determined. The Government recognizes the value of these tests and bases its specification requirements on them.

Needed: Big Scale Leather Research. By C. Roberts. *Leather and Shoes*, **122**, No. 18, 14 (1951). A thought provocative address on the need for large scale comprehensive research within the tanning industry.

Tanning Research. By R. Lotz. *Leather and Shoes*, **122**, No. 18, 28, (1951). An address.

Mold and Army Upper Leather. By R. M. Koppenhoefer. *Leather and Shoes*, **122**, No. 18, 30 (1951). Army shoes which had undergone extended storage in the South Pacific deteriorated considerably. The chrome retanned uppers not only lost strength, but the grease content was reduced to unusually low levels. In a preliminary study to determine whether the various stuffing components would evaporate, (an accelerated test involving heating of the components for 300 hours at 210°F.) it was found that the hydrocarbons lost not over 10 per cent of their weight. The natural fats were not volatile. Analysis of the shoe uppers showed a preferential loss of the fatty components of the stuffing mixture. In every instance of deterioration, mold growth was pronounced. These facts fit into the conclusions of Kanagy and Barghoorn that mold can decrease the grease content of leather, that fatty greases are readily attacked by molds, whereas hydrocarbons are not similarly affected, and that leather deteriorates as shown by loss of tensile strength. These facts emphasize the desirability of adding an effective fungicide, such as para-nitrophenol, to the leather.

The Importance of Physical Testing of Leather. By W. T. Roddy. *Lea. Manufacture*, **62**, No. 10, 9 (1951). An address on the subject.

East Indian Tannage. By P. H. Rao. *Tanner*, **5**, No. 6, 15 (1950). Tanning is carried out as a major cottage industry. The chief tanning materials used are Avaram for skins and wattle for hides, myrobalams being used for the final tannage. The white stock is laid down in open pits, and bark strewn between each skin. New Avaram shows a tannin content of 15-19 per cent, and the spent bark from the pits will show 6-9 per cent. A typical new bark will analyze as follows: moisture 10 per cent, tannin 18.6 per cent, nontannins 10.4 per cent, and insolubles 61 per cent. Analyses are given to show that successive leachings are more economical than single leachings, the latter leaving almost twice the amount of tannin in the spent bark as the former does.

Dressing and Dyeing Fur Skins. By M. Banerjee. *Tanner*, **5**, No. 10, 23, No. 11, 22; **6**, No. 1, 26 (1951). Fur skins are soaked only for a time sufficient to rehydrate them. Fresh skins are soaked but one to two hours, dry skins considerably longer in a 0.125 per cent sodium hypochlorite solution. After fleshing and thorough washing, the skins are given a pickle of salt and sulfuric or formic acid. About 2.5 per cent of formaldehyde is added to the pickle bath. Following this treatment, the stock is treated with retanning oils such as fish and linseed, and egg yolk. This is known as the Leipzig process. In alum dressing it is customary to immerse the skins overnight in a solution containing 4 parts potash alum, 6 parts salt, and 100 parts water. Pelts dressed in this manner would be thin were it not for

the subsequent treatment with egg-yolk and flour, or a combined alum-oil treatment with tanning paste brushed on the flesh. The paste consists of 3 parts alum, 1 part salt, 6 parts flour or French chalk and 3-4 parts egg-yolk. Alum dressed skins are less stretchy than Leipzig dressed pelts. They can be stretched appreciably when wet and retain their stretched shape when dry. They are heavier than the Leipzig skins. Bancoral A, a proprietary product which appeared in 1936, contains 30-32 aluminum oxide and has a basicity of 50. It is free from neutral salts and is used similarly to chrome. The stock does not have to be pickled, but in such case gives a leather of insufficient stretch. A better method is to pickle the stock for 2 to 3 days, then add 10-15 grams Bancoral A and 40-60 grams salt per liter of water. pH of the liquor is 2.5 to 3.5. If it is found necessary to neutralize the pelts, this can be done with bicarbonate. Formaldehyde tannage of pelts is accomplished by first pickling, then treating in a 1 per cent solution of commercial formaldehyde, and after an hour adjusting the pH to 9. Tanning is completed in 3-4 hours in the paddle. Skins are then drained and oiled on the flesh with a 50-50 sulfonated cold-water mixture. Vegetable dressing in a weak solution of gambier, myrobalams, wattle or other extracts can follow after chrome or alum tannage. Such skins are thick, soft and less stretchy. In the retannage, the hair gets more or less tinted. Gambier tannage is accomplished by painting the flesh with a paste consisting of 1.0 pound aluminum sulfate, 1.0 pound salt, 1 liter of water, 30 ounces gambier and 2 gallons of water containing sufficient flour to ensure a thin paste. The flesh is given 2-3 coats, and when the stock is dry it is given 2-3 additional coats. It is then rinsed with 1.0 ounce borax per gallon of water and given the usual fat liquor. Chrome tanning is done in a 3-4 per cent Cr_2O_3 solution with basicity of 33 per cent. It is accomplished in 4-5 hours. Stock is horsed up over night. Killing is necessary on unbleached skins in order to remove surface grease prior to dyeing. This is done with a solution of ammonia, salt and sulfonated oil. They are then rinsed with water and finally with a 0.1 per cent acetic acid solution. Another killing formula consists of an aqueous solution of ammonia and sodium hydrosulfite. Dyeing can be done at temperatures ranging from room to boiling. Furs and wools require acid dyes, the quantity ranging from 0.5 to 2.0 per cent on pelt dry weight. Acid dyes are exhausted with an equal amount of formic acid. Fur and wool skins should be oiled on the flesh only so as to avoid any gummy residue in the fur or wool. A satisfactory oil mixture, applied by swab or spray, consists of one part sulfonated oil, one part neatsfoot, 3 parts ammonia water and 5 parts sulfonated neatsfoot oil. Another oiling mixture consists of 2.5 parts mineral oil and 2.0 parts sulfonated cod.

Histological Study of Leather Manufacture I. By B. M. Das and S. K. Mitra. *Tanner*, **6**, No. 1, 14 (1951). An article on the histological study of leather manufacture, with Part I devoted to hide structure. The article is illustrated with photomicrographs.

Growth and Development of Tanning in Pakistan. By I. Islam. *Tanner*, **6**, No. 1, 21 (1951). At the time of partition, except for Batas, there were but four small tanneries in East and West Pakistan. Since then quite a few tanneries have been started, so that at least nine are now operating. Both vegetable and chrome leather are being produced.

Acid-Salt Control in Sole Leather Tanning. By J. C. Sen. *Tanner*, **6**, No. 1, 23 (1951). The control of salt and acid content of a tan liquor is more critical than the control of pH alone. The total acid content is responsible for the acid swelling effect of the liquor, and the salt content also regulates the swelling effect. British tanners have successfully replaced an appreciable percentage of pyrogallol with catechol tannins by a judicious control of the acid-salt contents of their tan liquors. An example is given of a case on record.

Mixture	Mimosa	Chestnut	Myrabs	Valonia	Reduncta	Queb.	Mgm. equivalent Acid	Salt
A	19	62	17	2	0	0	440	250
B	19	39	21	11	6	4	385	155
C	23	21	32	5	13	6	320	265
D	24	11	44	0	13	8	410	290
E	25	0	49	0	16	10	450	225

Liquor A was a normal prewar mixture. In B 1/3 chestnut was replaced with myrabs and valonia, but the leather was just as good. In C the chestnut was reduced another third and replaced by reduncta. The free acid content fell, but the salt increased and the leather was too soft. Mixes D and E were satisfactory. Leather most resistant to wet heat is tanned with liquors having the highest salt-acid ratio, while leather least resistant to wet heat is tanned in liquor containing more acid and comparatively little salt. A British firm successfully manufactured a chestnut substitute by wilful addition of organic acids to mimosa and bringing the acid-salt content in line with chestnut extract.

Some Aspects of the Pakistan Tanning Industry. By I. Islam, *Tanner*, **6**, No. 2, 15 (1951). The author describes the kinds and quantities of hides available in Pakistan. The vicissitudes of the hide market, scarcity of skilled labor and the lack of technical personnel are dealt with.

Resorcinol Tannage. By J. C. Sen. *Tanner*, **6**, No. 2, 19 (1951). Resorcinol is condensed with formaldehyde to form a long chain polymer. The product can be formed on the fibers of the pelt, whereby it does not need to be solubilized by sulfonation. The author first pickled pelt, then drummed it in resorcinol and water, followed by the addition of formaldehyde to the drum, and finally followed with hydrochloric acid. Retention of the pelt in the drum over night in contact with the liquor, followed by neutralization the following morning, completed the tannage. The leather resembled well filled, plump, vegetable tanned leather. It finished out soft and flexible with a yellowish color which did not darken on exposure to light. Although the leather appeared plum, nevertheless little weight was added to the pelt weight by the tannage. It is suggested that this synthetic tannage might be used wherein sulfonation is not required.

Modification of Collagen and Its Bearing on the Theory of Chrome Tannage. By A. Seetharamiah. *Tanner*, **6**, No. 4, 17 (1951). Methylated collagen was found to fix but little chrome, thus lending weight to the theory that the free carboxyl groups of collagen are responsible for the chrome fixation.

Potentiometric Titration Curves of Indian Tan Stuffs. By A. L. S. Rao and R. Selvarangan. *Tanner*, **6**, No. 4, 19 (1951). Weak tan liquors (20°Bk.) prepared by soaking the raw tanning materials in water for 24 hours, were titrated by the Atkin and Burton potentiometric method. Materials examined were myrobalam nuts, myrobalam extract, divi divi, mangrove, wattle, babul, avaram and konnan. The milligram equivalents of weak acids, salts of weak acids, ratio of weak acids to their salts, and buffer index of these materials are recorded in tabular form.

Investigations on East Indian Tannage of Kips. By A. L. S. Rao and R. Selvarangan. *Tanner*, **6**, No. 4, 20 (1951). There are about 500 tanneries producing East Indian skins and kips concentrated in South India. They are mostly of the cottage type. The leather is an important source of foreign exchange to India. Madras half-tanned leather is preferred because of its light tannage and because it is easily stripped by the foreign carrier for retannage with vegetable liquors or chrome. Avaram is the bark usually employed. Skins are left in the bark liquor for about two weeks after which they are given a myrobalam liquor for three days. Analyses and buffer indexes of the avaram and myrobalam liquors are given.

Use of Masking Salts in Chrome Tanning. By A. L. S. Rao. *Tanner*, **5**, No. 3, 15, No. 4, 16 (1950). The author gives a review of the literature on the use of masking salts in chrome tannage.

Syntans, Their Development and Use in the Tanning Industry. By S. G. A. Wise, *Tanner*, **4**, No. 2, 16, No. 3, 17, No. 4, 13, No. 5, 17 (1950). An article on syntans, their use and properties.

Water and Its Importance to South Indian Bark Tanning Industry. By A. B. Narayanan. *Tanner*, **5**, No. 5, 16 (1950). Because of the prevalence of bacteria and organic materials in subsoil waters, the summer temperature of the water, and the weakness of bark liquors (9°Bk.), it is essential that lime be not removed from the inner hide fibers before tanning, and that the hides be not bated if blisters are to be avoided.

Studies on Hide Beetles I. By B. M. Das and S. N. Sen. *Tanner*, **5**, No. 5, 12 (1950). Two kinds of hide beetles have been studied and a description of them presented. It is proposed to make a detailed study of their life cycle.

Standardization of Leather. By S. Raja. *Tanner*, **4**, No. 12, 12; **5**, No. 1, 9, No. 2, 8 (1950). The author recommends comprehensive standardization with respect to raw hides and skins, crust and finished leathers, and leather goods. The latter would include footwear, luggage, and industrial leathers.

Double Bath Chrome Tanning in Theory and Practice. By S. Sen. *Tanner*, **4**, No. 12, 27; **5**, No. 1, 17 (1950). The author first gives the theory of two-bath chrome tanning and follows this with description of tannery procedure. Following is the recommended process. Soaking: Drum in 400 per cent water and 10 per cent salt for 30 minutes. Wash in running water 15 minutes and pit soak over night. Liming: Drum 15 minutes the first hour and 5 minutes each successive hour throughout the day in 300 per cent water, 5 per cent slaked lime and 2.5 per cent sodium sulfide. Unhair. Delime by washing in paddle in running water 30 minutes, leave over night to bring to pH 8.5. Bate: Paddle bate for 30 minutes at 100°F. using 8 ounces per cent bate in 300 per cent water. Wash for 15 minutes, scud and again wash. First Bath: This consists of 5 per cent sodium dichromate on bated weight, 3 per cent sulfuric or 6 per cent hydrochloric acid, and 15 per cent water. Half the dichromate and acid are added in 100 per cent water, and after an hour the second half in 50 per cent water is added. Second Bath: In the same drum add 10 per cent sodium bisulfite to the contents of the first bath. The bisulfite is added in 3 portions at half hour intervals. The drum is run for 2 hours or until the skins change from a light yellow to a light greenish blue. pH should be 2.8-3.2, but if below this add soda ash. A violet pink color with diphenyl carbazide indicates the presence of unreduced dichromate. After tanning, horse up over night. Then wash in running water. Sammy, shave, dye, and fat liquor at 120°F. for 45 minutes.

Evaluation of East Indian Crust Leathers. By P. S. Briggs, *Tanner*, **5**, No. 3, 12 (1950). East Indian crust leathers have recently shown the presence of adulterants which have been sufficient to reduce the normally expected yield from these leathers. It is felt that the time is at hand when these crust leathers should be purchased by analysis.

Tentative Chemical Specifications of Pit Tanned Sole Leather Made from Indian Buffalo Hides. By B. N. Pal and P. K. Sarkar, *Tanner*, **5**, No. 3, 20 (1950). Because of the difference in hides, British specifications for sole leather do not apply to Indian buffalo hide sole leather, hence a set of chemical specifications for the latter has been formulated. Sampling is from butt, belly and shoulder, in 4 inch squares. Methods are given for determining moisture, fat, water solubles, soluble ash, total ash, hide substance, combined tannin and degree of tannage. Range of specifications on 14 per cent moisture basis is as follows: Fat, maximum 3.4; water solubles, maximum 12.5; insoluble ash, maximum 0.5; hide substance, 42-53; combined tannin, 25-36; degree of tannage, 55-80.

Cattle Improvement in India. *Tanner*, **5**, No. 7, 21 (1950). Cattle are raised in India for two purposes, namely, to provide milk, and to serve as draught animals. Some breeds are dual-purpose. India does not raise cattle for beef. The best milk producing breeds are the Sahiwal, Sindhi, Hariana, Tharparker, Gir, and Deoni. The Hariana and Tharparker produce excellent work animals as well, and are outstanding examples of dual-purpose cattle. The Kangayam, Amritmahal, Hallikar, Ongole, Kankrej and Gaolao are examples of breeds which produce high class draught animals. The Kankrej and Ongole possess more than average milking capacity. A third category is the nondescripts, representing over 60 per cent of the Indian cattle. The present policy is to upgrade this class into well defined breeds. Good cattle are generally found in dry areas and inferior cattle in areas of heavy rainfall. Thus the Punjab, Rajasthan, Saurashtra, Mysore, and drier parts of Bombay and Madras produce the best cattle. Nondescripts are found in areas of heavy rainfall like Assam, Bengal, Orissa and the Malabar Coast. The total number of breeds listed so far in Indian is about thirty-eight.

Technical Education (in India). *Tanner*, **5**, No. 7, 10 (1950). There are four tanning institutes in India, and the question arises as to whether it would not be better to consolidate these into one and consequently provide a more comprehensive education for the students. The schools and information pertinent to them are listed below:

Institute	*Year of Inception*	*Courses of Study and Annual Intake of Students*
Institute of Leather Technology, Washermaupet, Madras	Started in 1914 Closed down in 1931. Reopened in 1946	Diploma course: 3 years plus 1 year apprenticeship. Twelve students per year. Short and special courses.
Bengal Tanning Institute Calcutta	1919	Diploma course: 3 years. Twelve students.
Gov't. Tanning Institute Jullunder City, E. Punjab	Started in 1934. Reorganized in 1941.	A. Three-year course. B. Two-year course. Advanced Diploma course, 2 years; ten students.
Gov't. Tanning Institute, Bandra, Bombay	Started in 1939. Reorganized in 1948.	Artisan course, one year; twenty students.

Bating Agents for Hides. By B. M. Das and S. N. Sen. *Tanner*, **5**, No. 5, 20 (1950); No. 9, 23 (1951). Different strains of fungi were cultivated on bran and their proteolytic activity tested against casein as the substrate. Protease from *A. paracitucus* was found to be stronger than that obtained from *A. Oryzae* and *A. flavus* and fairly stable, whereas the other two varieties deteriorated slowly in activity when incubation was prolonged over a certain period. It is believed that the protease activity could be increased materially if cultures from the individual spores were tested and subsequently used as seed culture. Regarding the presence of ammonium salts in commercial bates, it is considered inadvisable to permit these to exceed 0.5 per cent in the bate water since they affect the salt linkages, disulfide linkages and hydrogen bonds, thus exposing the protein to proteolysis. While the presence of ammonium chloride to the extent of 0.1 per cent enhances tryptic digestion, the enzyme itself is a protein and can be denatured or inactivated by the ammonium chloride. Since the amount of ammonium salt present becomes a factor, three methods were examined for its determination as total and ammonia nitrogen. Alkali, magnesia and phosphate buffer distillation methods were examined and the last selected as the most satisfactory.

Tentative Chemical Specifications of Vegetable Tanned Leather Belting Made from Indian Buffalo Hides. By B. M. Das and P. K. Sarkar. *Tanner*, **5**, No. 11, 24 (1951). Samples are cut 6.5 x 2.5 inches from the butt and parallel to the back bone. Methods are given for determining moisture, fats, water solubles, soluble ash, total ash, hide substance, invert sugar, acidity and Epsom salts. A range of chemical specifications, expressed on the basis of fat-free leather with a moisture content of 15 per cent, are as follows: total ash, maximum 2.0; water solubles, maximum, 14; soluble ash, maximum, 1.0; hide substance, 35-50; invert sugar, maximum 2.5; Procter Searle acidity, maximum 0.7.

Mineral Oils in South Indian Tanning. By E. S. Subramanian and M. S. Ramakrishnam. *Tanner*, **5**, No. 12, 12 (1951). Mineral oils can be used for oiling where it is definitely known that such skins are to be finished with water pigment finishes or with nitrocellulose finishes using a sealer coat. The saving of edible vegetable oils effected by this change is a strong factor in its favor.

Studies on Pigeon Dung as Bate. By B. M. Das and S. N. Sen. *Tanner*, **5**, No. 12, 17 (1951). Experiments conducted with pigeon dung proved conclusively the presence of preformed filterable protease. To use the dung as bate, it is not necessary to infuse it in water for any length of time. The dung infusion can be used immediately for its protease action and this would probably save the leather from undesirable bacterial actions which are common in the use of dung bates. Actual bating experiments with pigeon dung suspensions in the preparation of fine leathers are in progress.

An Investigation on the Sulfonation of Indigenous Fish Oil Obtained from Madras. By B. M. Das and P. K. Sarkar. *Tanner*, **5**, No. 8, 15 (1951). A sample of indigenous fish oil was obtained on the Calcutta market, and used for the sulfonation experiments. After settling out the foots, the oil showed the following characteristics; acid value 44.5, iodine value 111.4, saponification number 184.8, specific gravity 0.899. In the first test two pounds of oil were cooled to 7°C. and one-half pound of sulfuric acid then added slowly with constant stirring. After standing over night, the treated oil was washed twice with 12 per cent sodium chloride. In other tests, glauber's salt was used, but found to be inferior to NaCl. Washing was followed by neutralization with caustic soda. Other neutralizing

agents, such as ammonia, potassium hydroxide and sodium carbonate, were tried, but from a cost standpoint, caustic soda was the most satisfactory. Neutralization was carried to the point at which the oil became clear and transparent. The same experiment was repeated on a larger scale, the same regard being given to maintaining a temperature of 5°-10°C. during sulfonation and washing. From 4 to 6 per cent caustic soda on the original weight of the oil was required for neutralizing. Degree of sulfonation and total alkalinity were found to be 57.0 and 2.5 per cent, respectively. The product proved satisfactory as a fatliquor base in the manufacture of box and willow sides.

Colonial Development Corporation Projects. *Leather Trades Review*, **98,** 214 (1950). The Colonial Development Corporation is about to start work on two major development projects in Bechuanaland: (1) a cattle ranch on the Chobe Crown Lands in Northern Bechuanaland, and (2) an abattoir and freezing plant at Cobatsi together with a holding ranch on the Molepole Crown Lands in Southern Bechuanaland. The ranch will take 18 to 20 years to complete, will cover and area of 16,000 square miles, and will carry sufficient cattle for over 50,000 drawoff annually. The abattoir is designed to handle 70,000 head of cattle per year. The projects are being undertaken, not to increase meat supplies of Great Britain, but rather to meet the needs of Central and of South Africa for good quality beef.

Fourth Proctor Memorial Lecture. On Membrane Permeability. By E. K. Rideal. *J. Soc. Leather Trades Chemists*, **35,** 2 (1951). The author discusses three types of synthetic membranes, their characteristics, relation to natural membranes and factors governing their behavior. The three types are (1) a capillary system in which the two sides are connected by a system of capillaries, (2) a sheet of polymeric material, (3) artificial protein membranes. R. H. T.

Mold Growth On Leather As Affected By Humidity Changes. By C. D. Rose and J. N. Turner. *J. Soc. Leather Trades Chemists*, **35,** 37 (1951). It is now considered that humidity of surrounding atmosphere is more important in mold control than water content of the solids. Moisture requirement of molds varies from 75 to 95 per cent relative humidity. Experiments were run in which leather of low relative humidity was allowed to absorb water increasingly under controlled relative humidity; and a parallel run in which the water saturated samples were allowed to desorb under the same relative humidity values. It is concluded that mold growth can only take place on leather when its moisture content exceeds a certain critical level. In these experiments the required level was not reached in an atmosphere below 85 per cent relative humidity. It is deemed probable that, before germination can occur on a fibrous material, there must be moisture present in the capillaries. In other words there must be water present in excess of that molecularly bound. R. H. T.

Change In Length of Stressed Collagen Fibers With Time. By R. H. Hall. *J. Soc. Leather Trades Chemists*, **35,** 11 (1951). Under small tension steel wire shows elasticity, bitumen viscosity. A more complex class of materials, of which collagen is one, exhibits "creep". Primary creep delays elastic extension equilibrium and recovery. Secondary creep differs in being non-recoverable, that is, causes a permanent set. Ox cheek fibers were selected for the experiments. An apparatus for control of the temperature of the fibers under stress is described. Results show that both primary and secondary creep take place. The latter decreases with time. Raising the temperature initially increases rate of secondary creep, but it falls off with time as with lower temperatures. The results are briefly correlated with the theory of collagen fiber structure. R. H. T.

The Strength of Single Collagen Fibers Tanned Under Tension. By G. R. Nice. *J. Soc. Leather Trades Chemists*, **35**, 21 (1951). Experiments having shown that leather of increased tensile strength can be produced by maintaining the hide under tension during tanning, an attempt was made to determine whether any significant part of this increased strength is due to changes within the fibers. A considerable number of individual fibers were tanned under tension. Devices were used to keep the tension constant. Because of the great variation in cross section of the fibers, conclusive data is difficult to obtain. However, when all results are considered, it is concluded that there is strong evidence that collagen fibers tanned under tension are stronger than those tanned free. R. H. T.

Apparatus for the Measurement of Water-Vapor Permeability of Leather. By G. R. Nice. *J. Soc. Leather Trades Chemists*, **35**, 17 (1951). The method used for the determination of the water permeability of leather is to use the leather as a membrane separating air at two different known humidities. Usually the leather is stretched across the mouth of a bottle containing a solid desiccant. If the bottle is then held in an atmosphere of known relative humidity, the increase of weight of the bottle in a given time gives data from which the permeability may be calculated. However, if this is done with the bottles at rest with no means of moving air at leather surface, layers of stagnant air at the surfaces introduce significant errors. To remove the stagnant air an apparatus was designed to sweep the leather surface with a fan. At the same time the bottle is kept in rotation serving the double purpose of keeping the desiccant tumbling and ensuring motion of air inside the bottle. This apparatus gives satisfactory results with light leather, sole leather and leather coated with plastic material. R. H. T.

The Assessment of the Plumping Pressure in Pelt. By H. G. Wollenberg. *J. Soc. Leather Trades Chemists*, **35**, 42 (1951). The plumping of pelt is considered to be the result of one internal swelling pressure (P_s) due to hydration and two counteracting forces which tend to reduce the volume. These are the osmotic pressure of the external solution (P_1) and the internal pull of the fibers due to the intrinsic elastic stress. (P_m). If the original volume is V_o and the swelled volume V_e, the equilibrium may be expressed by the equation $P_s - P_1 - P_m = K \frac{V_o - V_e}{V_o}$. K is a bulk modulus of elasticity which is constant. $P_s - P_1$ must be greater than P_m to produce swelling. If less, shrinkage will take place. In measuring these forces a modified hardness tester is used to determine the actual depression with known loads. Data so obtained is used to get a $P_s - P_1 - P_m$ value by means of graphical extrapolation of percentage compression/log load curves. P_1 is measured by use of an artificial sausage skin which is assumed to have an ion permeability similar to that of an actual pelt. With P_s and P_1 experimentally determined, P_m may be calculated. Results are given for pelts in solution of sulfuric acid and sodium sulfate, citric acid and sodium sulfate and hydrobromic acid and sodium bromide, through a pH range from 2 to 5.5 and salt concentration from zero to 0.7 *N*. In general plumping pressure was greater the lower the pH. Pressure decreased with increase of salt concentration except with the lyotropic salt sodium bromide, which showed a decrease from zero to about 0.4 *N* and then an increase. Shrink temperature of the sodium bromide treated pelt showed a parallel variation. Incidental work on the osmotic pressure of tanning liquor demonstrated that a large part of the osmotic pressure is due to the tannin molecules present. R. H. T.

The Effect of Various Factors On Tannin Content In Native Populations of Black Wattle. By D. B. Duncan and P. J. Martin. *J. Soc. Leather Trades Chemists*, **35**, 54 (1951). Analysis of 137 black wattle barks collected in New South Wales showed that the district of growth had significant effect on the tannin content. R. H. T.

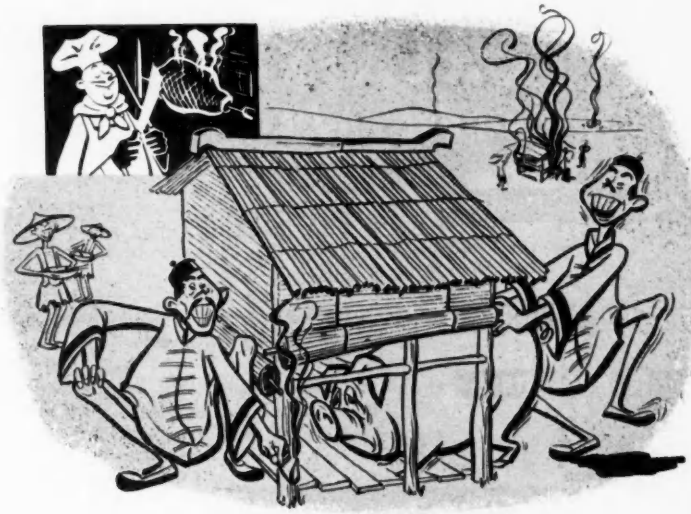
The Kinetics of Chrome Tanning. IV. The Effect of Basicity and Additional Masking Agents On Phthalate Masked Chrome Liquor Tannages. By P. S. Briggs. *J. Soc. Leather Trades Chemists*, **35**, 57 (1951). The effect of the use of more than one masking agent in chrome tanning is very hard to predict. In general the effect will depend upon the dissociation constant of the original acid, mass action effect from the amount present, specific properties of the anion such as its ability to form five or six-membered ring compounds and finally the position of the anion in the penetration series. Since the relative effect of these factors is difficult to assess, a series of tannages of hide with phthalate masked liquors was performed at 33 per cent, 42 per cent and 50 per cent basicities and with extra masking agents. Additional masking agents were sodium acetate, sodium formate, sodium sulfite and sodium oxalate. Tables are given showing the results obtained under the following captions; amount of each masking agent used, constant n, velocity of tannage at chromium equalling 1.0 and 0.5, average pH, precipitation point, contact drop, uptake periods at 50 per cent and 70 per cent and shrink temperature at chromium equals 0.5 and at 24 hours. In general it is concluded that modifications of phthalate masked liquor with salts of other weak acids produce effects which are not additive but are characteristic of amount, basicities and types. As a result there may be obtained accelerated or slower tannages, large or small contact drops, high or low velocity and long or short uptake. The rate of penetration as measured by shrink temperature at half exhaustion is shown to be diametrically opposed to the contact drop, which is taken to indicate development of large tanning complexes. Evidence presented does not give information about resultant leather qualities. R. H. T.

Investigation On the Chamois Tanning Process. By N. Klenow. *J. Soc. Leather Trades Chemists*, **35**, 67 (1951). Experiments were made testing the effect of the acid value of cod oil on chamois tanning. Two oils were selected having about the same iodine and thiocyanate values, but one having an acid value of 120 and the other only 1.15. By mixing these in varying proportions oils could be obtained with a wide range of acid values and practically constant iodine and thiocyanate values. Oils were tested by means of oxidation in a Mackey tester. Results showed that the acid value of the oil is very important. For practical tanning, oils below ten should not be used. On the other hand a combination of high acid value and high iodine value may give such rapid tanning that it is difficult to control. Oxidizing power increases with increase of free fatty acid up to a certain maximum beyond which further rise of acid value does not increase velocity of reaction. This maximum is shown to be at about 70 acid value. It was demonstrated that actual tanning coincides with increase in peroxide value. R. H. T.

Current Technical Tanning Problems. By J. A. Sagoschen. *Oesterr. Leder-Zeitung*, **3**, No. 1, 5; No. 3, 5; No. 4, 5; No. 5, 7; No. 6, 7; No. 7, 5 (1948). A discussion of the problems of, and progress in the Austrian tanning industry during and after the war. Raw material supply and quality and each step in the various tanning operations, for different tannages, are briefly considered. I. D. C.

The Theory of Tanning. By J. A. Sagoschen. *Oesterr. Leder-Zeitung*. **4**, No. 5, 8; No. 6, 6; No. 7, 6; No. 8, 6; No. 9, 6; No. 11, 13; No. 12, 9; No. 13, 8; No. 14, 12; No. 15, 7 (1949). A review, citing 121 references. I. D. C.

Extraction Equipment for Vegetable Tanning Materials. By A. Nagode. *Oesterr. Leder-Zeitung*, **3**, No. 8, 7 (1948). Different pump and piping arrangements for a six vat battery are shown. With only one pump for pumping and circulating liquors, only one vat can be emptied and filled per day. With two pumps a vat can be filled every 4 hours. I. D. C.



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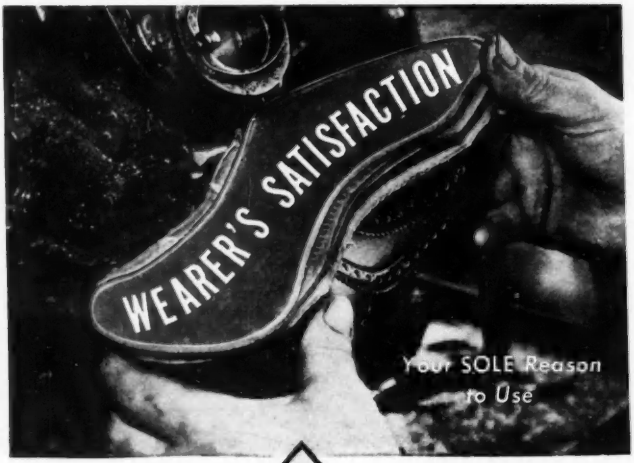

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